Assessing solvents effect for mitigation of asphaltene precipitation in South African Oilfields

MSC (50/50) Research Report

Prepared by

Alda Brigida Joaquim Saide

1561501

Submitted to

School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa

Supervisor: Dr. Diakanua Nkazi

20 June, 2018

DECLARATION

I declare that this research report is my own, unaided work. It is being submitted for a Degree of Masters of Science in Engineering at the University of The Witwatersrand. It has never been submitted to obtain any degree or examination at any other University.

Submitted by:

Alda Brigida Joaquim Saide

Signature of student:

Abstract

Asphaltenes molecules is one of the heaviest components in petroleum fractions that under reservoir conditions can be found either in colloidal form or dissolved in crude oil liquid phase. However, when variation in thermodynamic parameters such as temperature, pressure and fluid composition occur can lead to asphaltene precipitation phenomenon and posterior asphaltene deposition in oil wells, pipelines and processing facilities consequently, resulting in several damages along the petroleum chain as well as economical loss for oil and gas companies. Therefore, several studies have been developed to understand this phenomenon and eventually help to monitor and prevent its occurrence.

In relation to the present work, an experimental study will be developed in the crude oil samples of one of the South African oilfields to evaluate the effectiveness of different concentrations of two solvents (Salicylic acid and *Iso-* phthalic acid) in the asphaltene precipitation onset time when variation in temperature and fluid composition occur. This procedure combined with laboratory experiments have helped to define a solvent with great inhibitor capability to prevent asphaltene precipitation in this field and also, estimate the solvent inhibitor concentration and quantity to be used.

The results obtained in this study could thus allow the building of a clear picture about probable situations and/or stages to intervene for mitigation of asphaltene precipitation in South African oilfields.

DEDICATION

This thesis is dedicated to my parents as well as my husband for their unconditional support. I would also like to extend my heartfelt gratitude to my twin sister who encouraged me to keep fighting for my dreams.

> "*A good head and good heart are always a formidable combination. But when you add to that a literate tongue or pen, then you have something very special*".
>
> Nelson Mandela quotes

ACKNOWLEDGEMENTS

I would like to express my utmost gratitude and appreciation to;

God for unconditional protection and guidance during the hard times of my studies;

Dr Diakanua Nkazi, my supervisor and mentor during the entire duration of my studies;

Ms Ntokozo Dube for her tremendous support and guidance when I applied for my degree;

Prof. Michael Daramola for the rich content in lectures and advices given;

A warm and sincere gratitude is also extended to Canon Collins and GMT scholarship members for their funding, without this scholarship I could not have pursued my degree.

In addition, I would like to thank:

Mrs Janet Smith, Mr Bruce Mothibedi and Mr Mutlatsi Thali for their support and guidance during my lab work;

Ms Refilwe Moepya for her support during my SARA analysis;

Mr Famanda Elias Valoyi for providing solvents for my lab experiences;

Lastly, many thanks to all my lecturers and classmates for providing positive feedback and academic advices.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EQUATIONS

NOMENCLATURE

Abbreviations	**Description**
CNAC	Critical Nano-aggregate concentration
CII	Colloidal Instability Index
SARA	Saturate, Aromatic, Resin, Asphaltene
SPE	Society of Petroleum Engineers
BTX	Benzene, Toluene & Xylene
APE	Asphaltene Phase Envelope
SA	South Africa
EEZ	Exclusive Economic Zone
CBE	Coal Bed Methane
DBG	Deep Biogenic Gas
I.A.	Iso- phthalic acid
S.A.	Salicylic acid
n-C_7	n-heptane
US	United States
BP	British Petroleum
API^o	American Petroleum Institute gravity
SAOGA	South African Oil & gas Alliance
NGL	Natural Gas Liquid
HPM	High Pressure Microscope

NIR	Near-infrared spectroscopy
MSDS	Material Safety Data Sheet
N	Nitrogen
O	Oxygen
SD	Standard deviation
CO_2	Carbon dioxide
-OH	Hydroxyl functional group
-COOH	Carboxyl functional group
Tcf	Trillion cubic feet
Km^2	Kilometre square
g/mol	Grams per mole
mL	Millilitre
mm	Millimetre
g	Grams
rpm	Revolutions per minute
%	Percentage
$	Dollar
Vol.	Volume
h	Hours
min	minute
bbl/day	Barrels per day
ºC	Degrees Celsius

CHAPTER I: Introduction

1.1. Background information

Crude oil is defined as a colloidal sol, a colloidal solution composed by asphaltene micelles suspended in liquid hydrocarbons (Leontaritis, 1998).
Asphaltenes is one of the highest molecular weight fractions of crude oil, soluble in aromatic solvents and insoluble in n-alkanes (as n-heptane or pentane). In essence, the asphaltenes structure consist in both poli-aromatic and polycyclic rings holding alkyl side chains as well as heteroatoms as nitrogen, oxygen, sulphur and traces of metal (vanadium, nickel and iron) (Elochukwu & Mahmud, 2015).

Asphaltenes own a great tendency for self-association and the majority part of researchers had seen them as colloidal nanosized particles immersed in crude oil. In pure solvents, their aggregation tendency has been viewed as strong tendency of their concentration's level. At low level (below 50mg/L) in an aromatic solvent, asphaltenes could form molecular dispersed entities or oligomers of asphaltenes molecules. Roughly at 50mg/L CNAC (Critical nano- aggregate concentration), asphaltenes gradually develop structures with larger aggregated numbers named *nano- aggregates*. If asphaltenes concentration is greater than CNAC further clustering of existing nano-aggregate particles can happen (Haji-Akhari *et al.*, 2014).

The stability of asphaltene in crude oil is a matter of the utmost importance to keep under control in oilfields and it differs from field to field. In fact, asphaltene precipitation phenomenon does not occur in all crude oils; therefore, neither asphaltene content nor API° should be used as a measurement to predict its occurrence (Mahmoudi & Zare-Reisabadi, 2015). Studies have proved that Colloidal Instability Index (CII) test is by far described as one of the most accurate measurement of stable asphaltenes in crude. Crude oil has been described as a colloidal solution composed by pseudo components such as saturates, aromatics, resins and asphaltenes which expresses the stability of asphaltene in a fluid (Mahmoudi & Zare-Reisabadi, 2015; Karambeigi *et al.*, 2012).

Asphaltenes precipitation occurs at any point of oil production, transportation and processing owing to thermodynamic equilibrium destabilization in crude oil caused mainly by changes in pressure, temperature and oil composition (Hasssanvand *et al*. 2012; Wang, 2016). These variations in pressure, temperature and composition take place due to various processes such as primary depletion, either by injection of natural gas or carbon dioxide, acidizing treatment and commingled production of different fluids which could not be mixed (Zhang *et al*., 2007).

Upon asphaltenes instability mediated above changes, asphaltenes nano- particles (nano- aggregates and clusters particles) quickly increase their aggregate tendency, then form micrometer-sized particles and finally the phase separation occurs (Haji-Akhari *et al*., 2014), result in asphaltenes deposition along the production system (e.g. from inside the formation to pumps), blocking of pipelines and production facilities, decreasing in storage capacity, valves fouling, etc (Zhang *et al*., 2007; Wang, 2016).

The most successful method to prevent asphaltenes precipitation is operating at conditions outside the *asphaltenes precipitation envelope*. However, it is almost impossible due to a larger than expected drawdown in oil wells which lead to the reduction of the reservoir pressure below the onset pressure (SPE International, 2016) which has influenced into the temperature and crude oil composition.

Remedial treatment such as mechanical methods based on rod, pigging and wireline scrappers and physical methods as cutting are used to remove and clean asphaltenes deposits without high formation damage. However, the main drawback is that these methods are just limited to the wellbore, and in actual fact, they cannot remove asphaltenes deposits near wellbore plugging formation or from inside the formation to pumps (Dehaghani & Badizad, 2016).

Chemical treatments through aromatic solvents such as Benzene, Toluene and Xylene (BTX) are also used to remove asphaltenes deposits in wellbore and formation. However due to safety, health and environmental issues as low biodegradability, stiker regulations related to disposals, high toxicity, volatile-emissions limits agreement and flammability have made application of these solvents unattractive (Elochukwu & Mahmud, 2015). Therefore, alternative solvents have been studied to overcome these obstacles in relation to environment issues (Elochukwu *et al*., 2014).

The above-mentioned remedial treatments meant to remove asphaltenes deposits are widely applied in oilfields however most of them are expensive and mostly, plugging re-occur after a short time (Soltani *et al.*, 2010), therefore preventing asphaltene precipitation through solvent inhibitor is much better and attempts to find economical solution rather than applying different methods for asphaltene deposits removal (Karambeigi *et al.*, 2012).

Research has shown that preventing asphaltene precipitation based on changes in thermodynamic parameters as temperature, pressure and fluid composition is a great task and sometimes it is not achievable, mainly because asphaltene precipitation is considered reversible or not concerning to variation of thermodynamic conditions. In fact, there are two famous views describing asphaltene reversibility process in the crude oil. The ***solubility theory***, which describe asphaltene precipitation as a thermodynamically reversible phenomenon and ***colloidal theory*** which consider asphaltenes precipitation as an irreversible phenomenon (Abedini *et al.*, 2011; Leontaritis & Mansoori, 1987)
Furthermore, nowadays several solvents to inhibit asphaltene precipitation have been tested since these chemistries can act similarly as resins, both peptizing and keeping asphaltene under solution.

Recently, several case and experimental studies have been conducted to understand deeply asphaltene phase behaviour as well as find effective solvents to mitigate or remediate asphaltene precipitation in oilfields throughout the world. However, in relation to the available literature in Science Direct Journal there is roughly no study developed in South Africa related with asphaltene precipitation, therefore it is highly recommended to develop similar studies in South Africa oilfields since asphaltene precipitation phenomenon is a huge challenge without border in any petroleum field.

In the recent study, the effect of different solvents into South African crude oil samples was investigated based on changes in thermodynamic parameters such as temperature and fluid composition to monitor the delay time for asphaltene precipitation onset as well as verify the precipitation reduction after inhibitor addition in order to attempt to get a better understanding about when and how intervene to mitigate asphaltene precipitation in South African oilfields.

1.2. Problem statement

Several problems in the oil production systems caused by asphaltenes precipitation has motivated researchers to investigate various theoretical models and experimental methods in order to prevent the occurrence and bigness of this complex phenomenon still in its early stage (Panuganti, 2013).

According to Maqbool, (2010) and Meraikhi, (2015), asphaltenes are assumed to be dissolved in crude oil at high temperatures and pressures.
Asphaltene precipitation begins when variations in temperature and pressure occur due to loss of hydrostatic pressure since crude oil pumped in vertical systems up to wellbore causes the light components (e.g. methane) to expand, reducing consequently asphaltene solubility which leads the formation of unstable colloidal nano-aggregates. Once aggregation occurs, it leads to the problematic of asphaltenes deposition phenomenon on the inside walls of production systems, bringing a complex economic impact on crude oil production and processing. Moreover, studies have also shown that oil flow lines with low asphaltene concentration (1% weight) can lead several deposition problems rather than those with high asphaltene concentration (50% weight)., In other words, asphaltenes precipitation and deposition does not only occur because of changes in temperature and pressure but also due to other many factors such as asphaltene concentration and solubility, stability of asphaltene nano- aggregates, flow conditions, etc (Meraikhi, 2015).

To keep the conditions of asphaltene precipitation under control in crude oil different thermodynamic models of asphaltene phase behaviour have been studied and developed as function of temperature and pressures changes. However, studies have also proved that chemical solvents are considered the most successful and efficient approach to either make asphaltene remain under solution or retard asphaltene precipitation (Elochukwu *et al.*, 2014; Dehaghani & Badizad, 2016), since some chemical solvents present the most practical and economical inhibitory capability for asphaltene remedial treatment (Junior *et al.*, 2006).

It is notable that few studies about chemical solvents inhibitors already done have presented possibilities to identify and advance towards more sustainable solvents for mitigation of asphaltene precipitation. But due to the complicated nature of crude oil (which contribute to poor understanding about the phenomenon leading the destabilization of oil phase, aggregation and posterior precipitation of its asphaltenes) and insufficient experimental data of the effectiveness of these solvents in many crude oil, there is a need to develop more studies to estimate these inhibitors with as many different crude oils as possible to achieve consistent results (Karambeigi *et al.*, 2012; Junior *et al.*, 2006).

With the aforementioned reasons, researchers believe that any insight in ways for mitigating asphaltene precipitation that could be given through an enriched understanding of the crude oil phase behaviour would be useful and notable, but developing this understanding means building a scheme for studying multi-components mixtures as asphaltene molecules (Artola *et al.*, 2014).

1.3. Research questions

- What is the influence of variation in temperature and oil composition into asphaltene stability?
- Which kind of chemical solvents can be proposed to retard asphaltene precipitation?
- When and how to intervene for mitigation of asphaltene precipitation in South African oilfields?

1.4. Research objectives

The main objective of this work is to:

- Assess and test the effectiveness of two chemical solvents in South African crude oils when variation of temperature and crude oil composition occurs in order to either inhibit or retard asphaltene precipitation.

The present aim could be achieved through:

- Assessment of the impact of changes in temperature and fluid composition on asphaltenes solubility after addition of a precipitant (n-heptane);
- Investigation of the effect of different chemical solvents (salicylic acid and *iso*-phthalic acid) in crude oil samples;
- Testing inhibit capability of each solvent through addition of different concentrations in the crude.

CHAPTER II: Literature review

2.1.Asphaltenes properties and characteristics

Asphaltene is defined as class of hydrocarbons' components (Zhang *et al.*, 2007). According to ASTM D-3279-90 (IP143/90) test, it is considered as a solid which precipitate as long as an excess of n-heptane or pentane is added into the crude oil (Eigner., 2016).

Asphaltenes properties have been studied since before the drilling of the first commercial oil reservoir, in 1859. The term was introduced in 1837 by J. Boussingault when designated asphaltene as the residue of bitumen' distillation: insoluble in alcohol and soluble in turpentine. Nowadays, its definition is almost the same, insoluble in n-alkanes (e.g. n-pentane) and soluble in aromatics (e.g. toluene). In general, asphaltenes are dark-coloured, friable and have a complex structure which is normally polar with relatively high molecular weights aliphatic hydrocarbons (nearly 700 to 1000) and density of 1.2g/cm^3. In addition, they do not have a defined melting point (infusible crude oil component), however it could decompose when heated, leaving a carbonaceous residue (Zhang, 2007).

According to Eigner (2016) and Meraikhi (2015), asphaltene molecule is formed by a peri-condensed poly-aromatic skeleton holding alkyl linkages and aliphatic side chains as well as connected to a few heteroatoms (N, O and S) as show figure 1. In addition, they also show traces of heavy metal such as vanadium and nickel).

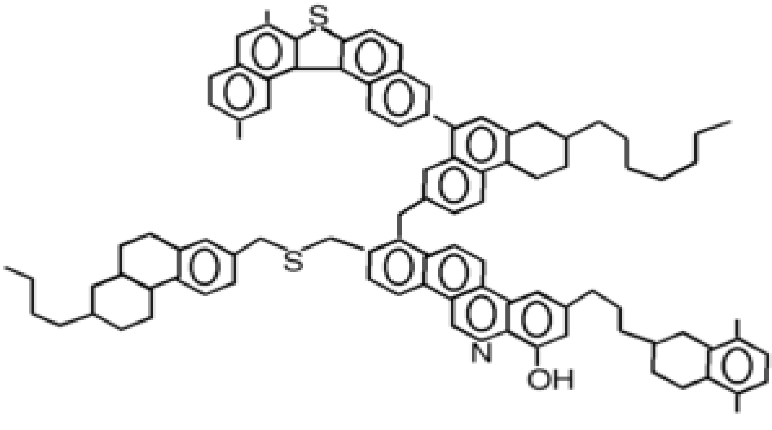


Figure 1: Hypothetical asphaltene structure. (SPE International, 2016).

Due to the natural characteristics of asphaltene chemical structure, asphaltene shows an intense tendency for self-association as well as cross-association with other aromatic components as resins molecules in crude oil however, the asphaltene- resins association is still unclear (Shirani *et al*., 2012a; Zhang *et al*., 2011). Many studies have agreed that asphaltenes are normally dispersed by resins in crude oil and both are dissolved in oil phase by smaller aromatics that are considered asphaltenes solvents and also by saturates that are non-solvents for asphaltenes. Therefore, asphaltene is presented in crude oil as a hydrocarbon in a fragile balance that when disturbed it will precipitate and lead to deposition problems (Zhang *et al*., 2011).

2.2.Asphaltene precipitation phenomenon

According to the abovementioned researchers' viewpoint, crude oil is a colloidal system where asphaltene is a dispersed phase. Under reservoir pressure and temperature, asphaltene uses to be in colloidal suspension in which it is stabilized by resins. Basically, asphaltene has either a positive or negative charge, depending on the fluid composition. Resins have a strong tendency to bond themselves to asphaltenes as well as attract opposite charges that make a protective shield around the asphaltene. When this protection is destroyed, asphaltene precipitation occurs since crude oil stability is highly dependent on force balance between adsorbed resins and asphaltenes (Shadman *et al.*, 2012).

Asphaltene precipitation is defined as the agglomeration of nano-particles, followed by the formation of a solid phase out of a liquid phase (crude oil) generally as a function of changes in thermodynamic parameters such as temperature, pressure and fluid composition (Rastagoo & Kharrat, 2017). This phenomenon has been considered a major assurance challenge creating notable loss in the economic and technical areas of petroleum industry (Dehaghani & Badizad, 2017).

The asphaltene deposition process occurs after its precipitation happens, since only suspended asphaltene particles can deposit and block the porous media. Therefore, to depict clearly asphaltene precipitation phenomenon, the Asphaltene Phase Diagram/Envelop in figure 2 must be well understood (Almehaideb, 2004).

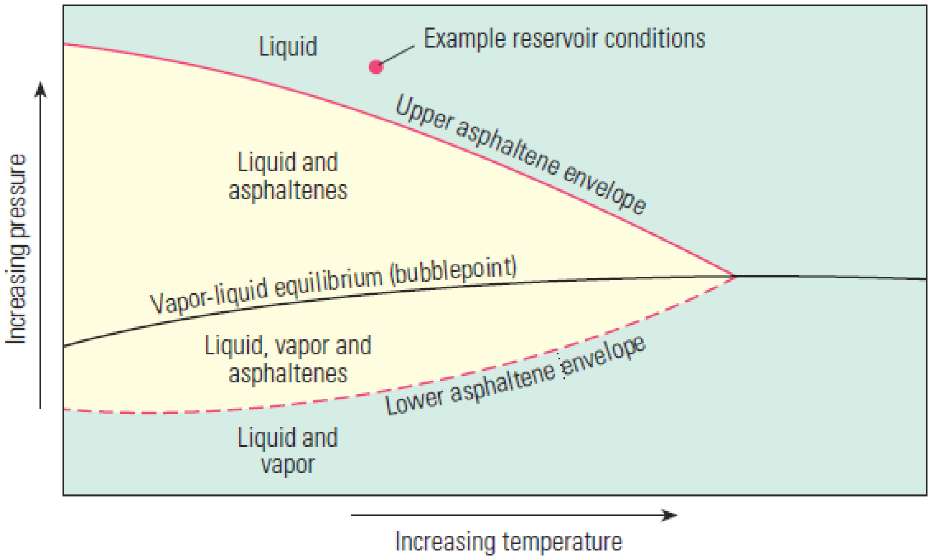


Figure 2: Asphaltene Phase Envelope (APE). (Zhang et al., 2007).

APE is designed in pressure-temperature space, so the APE (*red curve*) indicates the stability zone for asphaltene remains in solution. For instance, in reservoir conditions (*red dot*) primary depletion leads to pressure drops. When asphaltene reaches the asphaltene precipitation onset (*red continuous line*) the least soluble asphaltene will precipitate. As pressure keep decreasing more asphaltene will precipitate and reach its maximum at bubble point (*black curve*) while gas is being released from solution. Reducing more the pressure, sufficient gas is released out of the system and asphaltene re-dissolution in crude oil starts below the bubble point until reach the lower APE (*red discontinuous line*), changing consequently the fluid composition (Zhang *et al*., 2007; Almehaideb, 2004).

Efforts for asphaltene precipitation and deposits remediation in oilfields have been studied in three directions:
(*i*) Investigation and creation of theoretical models either to predict asphaltene precipitation/deposition or mitigate this phenomenon (i.e. Kokal *et al*., 2005, Soltani *et al*., 2010; Tavakoldavani, & Ashoori, 2017); (*ii*) deep studies of asphaltene phase behaviour in crude oil and model systems (i.e. Ting, 2003; Panuganti, 2013; Meraiki, 2015) and (*iii*) investigation of chemical solvents that can be used to inhibit, disperse or remove asphaltene precipitation (i.e. Junior *et al*., 2005; Kashefi *et al*., 2016; Dehaghani & Badizad, 2016; etc).

2.3.Asphaltenes stability

According to Speight, J. (1992), the stability of crude oil can be described by four phases systems: saturates (S), asphaltenes (A), resins (R), and aromatics (A). Therefore, data from SARA analysis are applied to cross-plots of saturate/aromatic ratio as well as asphaltene/resin ratio as shown in the figure 3.

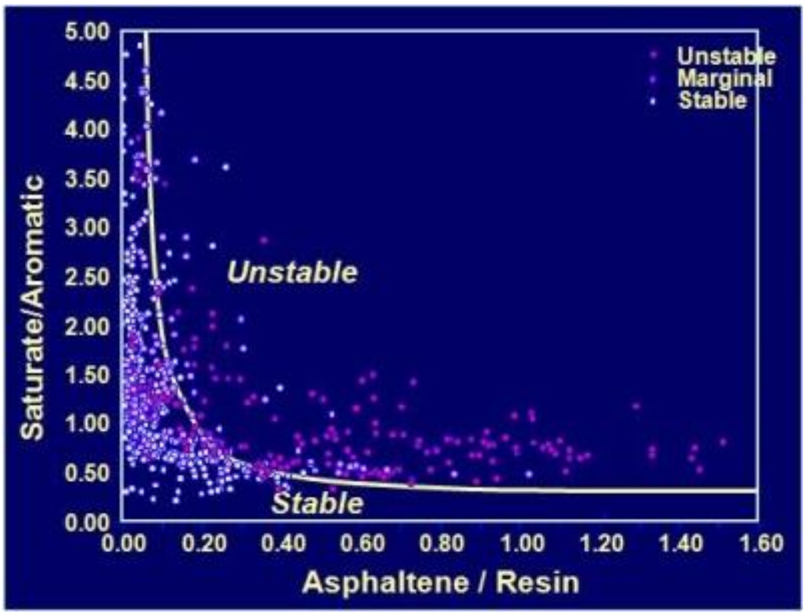


Figure 3: Assessment of asphaltene stability through SARA data. (Eigner, M. 2016)

In general, the saturate/aromatic ratio indicates the solvency power for asphaltene; it is as higher the aromatics as stronger the asphaltene solvency. Consequently, more stable asphaltene will be in the fluid. On balance, asphaltene/resin ratio describes the colloidal state of asphaltene in the oil. Therefore, as lower asphaltene/resin ratio is, a better colloidal stability will be achieved.

In fact, the stability of crude in petroleum oilfields is a matter of utmost concerning to oil companies and it can change from fluid to fluid. Neither asphaltene content nor API° gravity of crude can determine the tendency of asphaltene precipitation. One of the most precise measurement of asphaltene stability is the Colloidal Instability Index (CII) since it considers the four phase systems in the crude oil (Mahmoudi & Zare-Reisabadi, 2015).

Asphaltenes normally remain in solution in under-saturated crude oil (below virgin reservoir condition). However, during crude oil production, processing and transportation asphaltene can become instable due mainly to changes in pressure, temperature and fluid composition (Eigner, 2016). Thus, different effects could occur.

a) Effect of pressure

Changes in pressure leads to asphaltene phase separation mostly in light oil roughly at its bubble point or above since pressure has a big power on the flocculation of asphaltene. As crude oil surges inside the tubing, the pressure slowly drops and the oil components (light and heavy) expand depending upon their compressibilities (Eigner, 2016). This result in increasing the molar volume of the lighter components in the oil, increase their effect to precipitate stable asphaltenes. At low pressures (below the bubble point) asphaltene tends to stabilize since the majority part of the precipitants (methane, ethane, nitrogen, etc) have already evaporated from the liquid (Ting, 2003).

b) Effect of temperature

Whether variations in temperature will cause either asphaltene precipitation or solubilization are still under debate. Many field experiences and laboratory studies had shown that the effect of thermodynamic parameters such as temperature in asphaltene destabilization is not clear yet (Mohammadi *et al*., 2016; Zubair *et al*., 2015).

According to Maqboot *et al*. (2010) the impact of temperature on stables asphaltenes can be complex and various effects can be identified. Through their studies, they have shown that at high temperature the precipitation onset time for asphaltenes is shorter while their solubility is higher owing to the difference of viscosity, influence of hydrocarbon’s expansion, oxidation of crude oil and evaporation of light hydrocarbon (effects whose occur when temperature rises). On their argument, they had explained that for example, high temperature will change the fluid composition since when oil is heated, its lighter fractions (mostly alkanes) will expand and effectively decrease the oil solubility parameter, consequently reducing asphaltene solubility into the oil. Therefore, they concluded at high temperature due to the lower asphaltene solubility, asphaltene particles aggregation will be faster and the precipitation onset time will be shorter. In this case, oil wells with little asphaltene content will easily precipitate at high temperature.

Hassavand *et al*., (2011) had evaluated effect of temperature on asphaltene precipitation through visual methods (NIR and MPM) and revealed that the asphaltene precipitation phenomenon begins by the formation of initial solid nuclei, followed by growth of the solid nuclei size and then, solid particles precipitate out of the oil liquid phase. Furthermore, they had observed asphaltene instability in the reservoir oil (at 145.72, 143 and 90ºC) and concluded that decreasing temperature, increases the onset of asphaltene precipitation pressure above bubble point pressure, in other words, increasing in temperature leads asphaltene precipitation phenomenon to occur at low pressures.

In addition, Amhadi *et al*. (2014) have investigated the effect of temperature and pressure on the reversibility of asphaltene precipitation. Their study was divided in two parts: (*i*) Pressure's reduction from initial reservoir pressure to roughly saturation pressure and monitoring asphaltene content when re-dissolution of asphaltene occurs at reservoir temperature and, (*ii*) analyzing of precipitated asphaltene in both processes (precipitation and re-dissolution) at different pressures and temperatures. The results revealed that above bubble point pressure asphaltene precipitation was practically reversible in two crude samples and partial reversible in one sample (A) with regard to the temperature. Thus, pressurizing was considered a great method to reduce asphaltene precipitation in both heavy oils and increasing temperature had solved precipitation problem in crude oil sample A.

Although the abovementioned researches have presented strong discussion about different approaches to identify the impact of temperature on the kinetics of asphaltene precipitation, they only studied the effects of temperature when a precipitant (*n*-heptane) is added, not extending in case that a solvent (e.g. an aromatic) is added. Furthermore, it is notable that the effect of temperature is still unclear and more studies should be done since this parameter is extremely important for asphaltene stability in crude oil.

c) Effect of fluid composition

Pressure and temperature variations are not the only main factors that cause asphaltene precipitation, oxidation, electrical fields (Manfred, 2016) mixing incompatibles crudes in different points (e.g. wellhead, flowlines, pipelines, fluid treatment facilities, etc), miscible and CO_2 flooding, gas lift application trough rich gas and acidizing stimulations increase the potential for asphaltene precipitation occurrence in oil fields and posterior deposition as show figure 3 (Rastgoo & Kharrat, 2017; Eigner, 2016). Adding one or more compounds with molecules that are different of resins and asphaltenes sizes and structures lead to changes in the solubility parameter (Rastgoo & Kharrat, 2017)

Figure 4: Effects of different parameters on asphaltenes precipitation. (Eigner, M., 2016).

2.4.South Africa oilfields

In light of the literature shown, South Africa presents very little amount in terms of proven oil and gas reserves (Newman, 2016; SAOGA, 2014; SAMSA, 2011.; Petroleum Agency SA, n.d.). In essence, oil and gas exploration in this country started in 1913; however, on the contrary there were no good results. In 1990s, prospectors and exploration companies had found local useful oilfields trough application of modern survey techniques although the amount of oil and gas discovered was assumed globally insignificant. Recent studies in SA have shown that petro geology for oil seems modest but on the other hand, the prospects for natural gas, conventional gas, shale gas or coal bed methane gas looks to be more promising (Newman, 2016).

The relative under-usage of gas in the country is consequence of the presence of abundant coal resources that allows SA to produce petroleum, its by-products and electricity as well, cheaply based in coal. However, decreasing coal resources and the proportional cost to generate electricity and produce petroleum in financial and environmental terms will force SA to branch out its energy sources, a process already under development nevertheless (SAOGA, 2014.).

Geographically, SA has an Exclusive Economic Zone (EEZ) with oil, gas and other minerals comprises a total of ~1 535 538Km^2 which includes areas close to the mainland (1 068 659Km^2) and areas surround Prince Edward Island (466 879Km^2). However, the zone under exploration as well as used for production of oil and gas consists of a total of ~422 600Km^2 and just spreads the surface close to the mainland while areas next to South African Islands are not being explored (SAMSA, 2011).

Figure 5: Zones under exploration in SA. (Petroleum Agency SA, n.d.)

Fundamentally, the Orange Basin (West Coast) is by far the largest volumetric South Africa’s offshore basin. It is already under exploration with a well with a total up to 4000 Km^2 and many petroleum systems being operating. In addition, two prospective oilfields (Bhubesi and Kudu) with multi-trillion cubic feet natural gas reserves had been discovered recently. Nonetheless, still a large area of the east coast of SA remains under exploration although provides promising exploration potential estimated in a total of multibillion barrel range of hydrocarbons (SAMSA, 2011).

Table 1: Oil & gas exploration and production areas (Petroleum Agency SA, n.d.)

Area	**Range (Km^2)**
West coast basin	191 600
East coast basin	107 000
Outeniqua basin	124 000
Total	**422 600**

a) Oil & gas statistics

Studies have shown that if offshore as well as onshore shale gas exploration proves to be successfully developed in SA; this country will have a huge supply of oil and gas which will diversify the country's energy mix (SOAGA, 2014)

Onshore exploration

- ***Conventional oil and gas***

Table 2: SA conventional oil and gas statistics (SOAGA, 2014).

	Production/ Reserves	**Share of the world (%)**
Oil production (bbl/day)	191 000	0.22
Proven oil reserves (million bbl)	15	0.001
Gas production (m^3/yr)	970 000 000	0.03
Proven gas reserves (m^3)	27 160 000	0.00001

- ***Unconventional gas***

According to different reports, South Africa has a notable potential for unconventional gas which has been discovered in form of coal bed methane (CBM) shale gas, therefore comprises a total of ~20-30 Tcf of CBM and ~390 Tcf of recoverable resources (SOAGA, 2014 & Newman, 2016) and as estimated by US Energy Information

Administration, South Africa is ranked between the fourth and eighth largest shale reserve in the world.

Table 3: SA unconventional gas statistics (2014).

	Resources/ Reserves (Tcf)	Global ranking
Coal bed methane(1)	20-30	12
Shale gas technically recoverable(2)	390	8
Shale gas potential(3)	30	___

(1)Energy Tribune, (2)US Energy Information Administration, (3)Petroleum Agency SA.

Offshore exploration

Owing to the depth of the potential reservoirs and ocean currents strength, costs for offshore exploration in South Africa had been previously limited. However, advanced exploration's technology coupled with the demand of SA to branch out its Energy sources has been increasing interest regarding to offshore exploration in South Africa's coast, already with 20 exploration issued to date (SAOGA, n.d.).

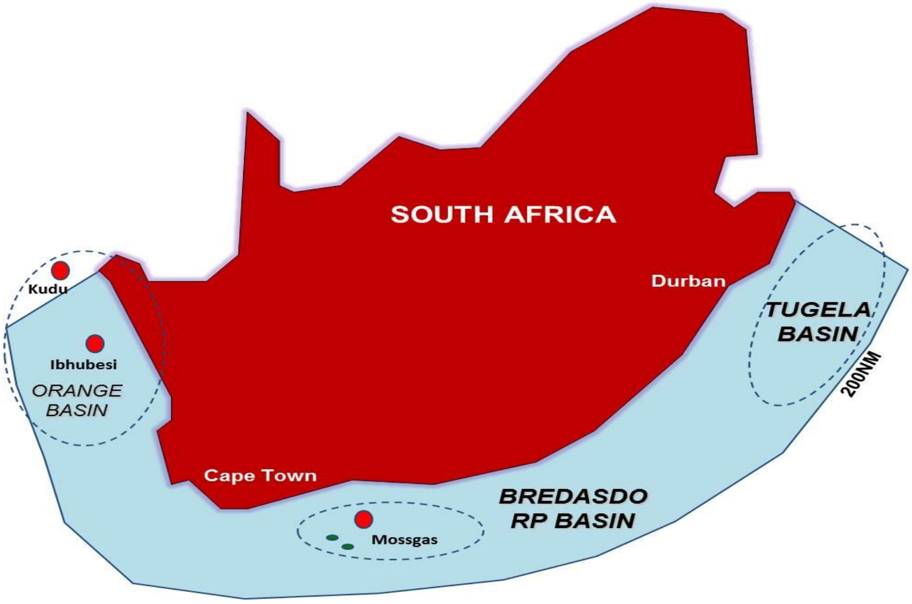


Figure 6: Map of SA offshore basins. (SAOGA, n.d)

b) Prospects and future development

Shale gas

Studies developed by Petroleum Agency revealed Karoo basins as the most prospective zone for shale gas exploration in this country owing to the existence of deeply buried, thermally mature shale. Moreover, oil and gas presence across this field indicated an active petroleum system prospect with multi-play potential since the huge presence of pyrobetumen in Southern side of this area shows an original oil-prone rock.

The volume of gas in place in this region is definitely uncertain; nonetheless different scenarios had estimated a technical recoverable volume from ~30Tcf up to 500Tcf.

The total economic value of Karoo shale gas will be known when a recoverable statistically volumetric number of reservoir flow rates have been measured. However, in order to SA becomes one of the major shale gas producers around the world, a high notable investment in infrastructure will be required (Petroleum Agency SA, n.d.).

Furthermore, the team leader geoscientist at seismic surveys provider spectrum Intawong, A. as cited by Paraskova, T., (2017) had suggested a giant future discovery offshore fields at Outeniqua basins since previous discoveries had indicated recoverable volumes range to 314 million barrels of oil equivalent.

Coal Bed Methane (CBM)

CBM is a source of natural gas that is produced and kept in coal beds structures. CBM can be found in coal in three forms: free gas, dissolved gas (gas dissolved in the water in coal) and absorbed gas (gas absorbed on the solid area of coal). In fact, as coal shows to have large internal space, it can store roughly six to seven times more gas rather than the volumetric amount stored in a rock of conventional gas reservoir.

Clearly, SA presents a huge amount of methane gas in coal which can be found in underground coal mining. Recently, methane has been considered an utmost significant source of natural gas all over the world. In SA, Coal reserves are located in Karoo basins as well as in further North at fault bounded rift basins. Both basins prove to be a potential for a great promising future source of energy (Petroleum Agency, n.d.).

CBM exploration in SA keeps growing with 25 exploration rights awarded until now and different oil and gas companies applying for rights as well (SOAGA, 2014)

Deep Biogenic Gas (DBG)

DBG is defined as an unconventional gas generated in highest depth through microorganisms' respiration and fermentation processes (microbial gas) and migrates to the surface through natural fractures systems, faults and dykes. Generally, the gas is composed mostly by methane, other hydrocarbons and Helium too.

In SA, DBG is considered the hydrocarbons generated in the deep mines along the Witwatersrand basin. Presently, the greatest promising fields in Witwatersrand basin for DBG exploration are situated between the Free State and Evander Goldfields (Petroleum Agency SA, n.d.)

Refining

According to SAMSA (2011) report, SA provides the second biggest refining capacity in the African continent, producing 703 000 bbl/day of total oil, where 508 000 bbl/day is distributed to four oil refineries in SA, namely: Sapref and Enref (Durban); Chevref (Sasolburg); and Natref (Cape Town) as show table 4.

Table 4: SA refining capacity (SAMSA, 2011).

Refinery	**Location**	**Ownership**	**Capacity (bbl/d)**
Sapref	Durban	Shell (25%), Thebe investment (25%), BP (50%)	180 000
Enref	Durban	Engen	120 000
Natref	Sasolburg	Sasol (63.6%), Total (36.4%)	108 000
Chevref	Cape Town	Chevron	100 000
Mossel Bay GTL	Mossel Buy	Petro SA	45 000
Sasolburg GTL	Sasolburg	Sasol	150 000
Total capacity	__________	___________	703 000

2.5.Challenge and solution of asphaltene problematic

In oil and gas companies' operation, precipitation and formation of organic deposits is regular. Among the organic compounds that lead production problems, there are two main groups: Paraffin wax and asphaltene. Therefore, it is demanding to identify the predominant conditions under the occurrence of these deposits as well as the solution which can be mitigated in order to reduce several damages to the process (Chrisman *et al.*, 2012). In essence, asphaltene problematic is more complex to solve rather than paraffin problems. Asphaltene challenges may occur along the production chain but mostly occur inside the rock formation and downhole. While paraffin challenges on the other hand, normally occur in the upper part of production tubing and surface facilities. The balance of the evidence suggests asphaltene problems are more expensive to solve while paraffin problems can be settled with a reasonable cost (Leontaritis, 1989).

In actual fact, the amount of the asphaltenic problems and its economic impact throughout petroleum fields cannot be overstated (Leontaritis, 1998). In general, asphaltene can precipitate anywhere in the production scheme (Chrisman *et al.*, 2012); as result its precipitation can lead formation of asphaltenic deposits in reservoir rock and consequently damage the well's production by clogging the pores of the rock, flowlines and changing the wettability of the reservoir rock, which can be a huge problem since will lead to well losses (Zhang *et al.*, 2007; Chrisman *et al.*, 2012).

Furthermore, asphaltene precipitation and deposition can also occurs on the production lines, surface facilities and subsurface formations and remedial methods to remove it cost a lot of money as well as require all safety procedures to be in place because just any accident can lead to production line loss (Carnahan, 1989).

In refining, this phenomenon contributes to catalyst deactivation as well as formation of waste when thermal and thermo-chemical processing of heavy residues of crude oil occurs (Speight, 2001).

Overall, almost in all stages of production chain, processing and transportation systems asphaltene problematic can happen and consequently impact negatively into the companies' economy (Chrisman *et al.*, 2012).

Figure 7: Asphatenic oil deposition problem. (Eigner, 2016).

In fact, the seriousness of asphaltene precipitation and deposition is considered a global problem without borders. Several researchers have already reported many cases in different regions.

For example, according to some investigators alphatenic oil can be found in Nigeria offshore as well as Brazil offshore, including Brazil’s campos and Santos Basins.

Colombian field is also assumed to contain solid asphaltene although asphaltene problematic is more predominant in Venezuela. Mediterranean has shown asphaltene with similar behavior such as in Venezuela’s field.

North Sea, United States including Alaska, Central Asia, and Middle East contain asphaltene in those fields too. Canada and Russia also have reported asphaltenic oil fields. Egypt, the Suez, Kuwait (the Marrat reservoir) and Abu Dhabi (Zacum reservoir) have already reported asphaltene problems as A&W Map shows below (Leontaritis, 1989).

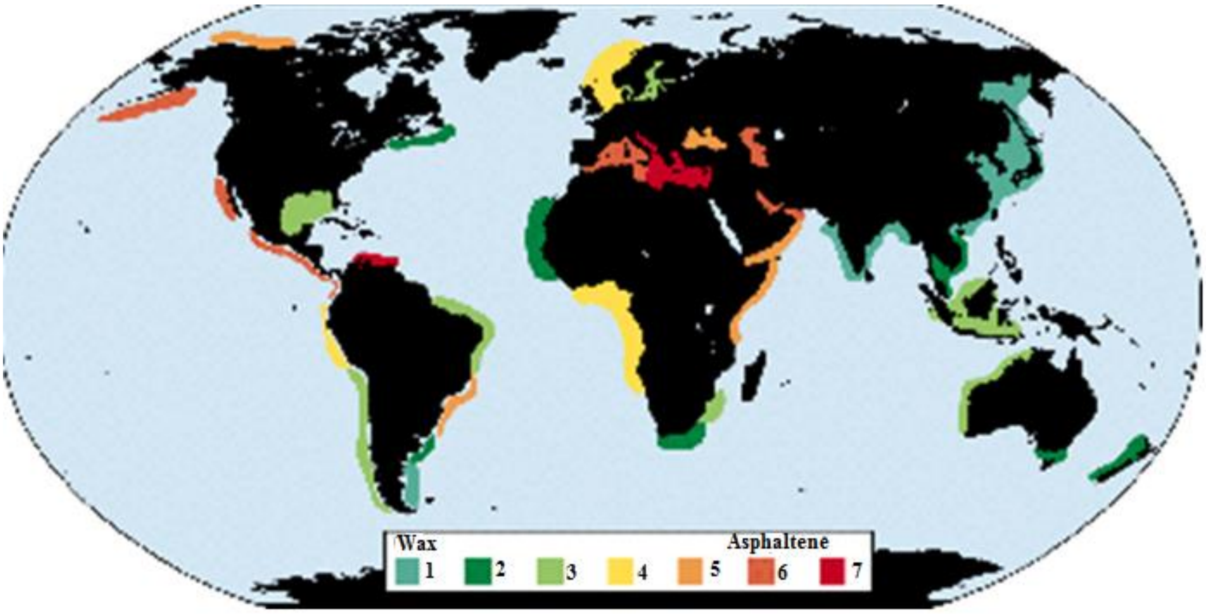


Figure 8: Asphaltene & Wax World Map- A&W Map. (Leontaritis, 1989)

According to the available literature, many study cases have been written and proved that application of inhibitor or solvents can bring good results from field to field.

For instance, Nalco Energy Service have introduced a treatment based on inhibitor mixed with an activator in oil fields with most asphaltene deposition problems in the globe such as Venezuela, the Persian Gulf, the Adriatic Sea and the Gulf of Mexico. In Venezuela, a severe volume of asphaltene deposits had plugged the production well during seven months of treatment. Effort through different remedial treatments was applied, costing nearly US $50 000 and two days of shutdown in the production. After Nalco apply is treatment based on an inhibitor plus an activator, the oil production rates grew and the well treatment reduced to every eight months. The gain was notable in an increment of 60,882 barrels per year and a return of more than 3% of the company’s investment (Zhang *et al.*, 2007).

Similar asphaltenic problem happened in the Adriatic Sea. The problem was discovered when the field was examined in 1993, results of tubing string tests revealed asphaltene deposition along 1,006m of the length tubing under the seafloor. Based on laboratory analysis of oil samples, asphaltene deposits were controlled through downhole injection of a solvent dispersant and eventually the well had operated for many years without any clogging challenge (Zhang *et al.*, 2007).

2.6.Asphaltene solvents inhibitors

Asphaltene inhibitors are long chain compounds that act as resin around asphaltene layer in order to avoid asphaltene precipitation occurrence when injected into the crude oil. However, some chemical inhibitors are actually considered chemical dispersants due the fact that they do not inhibit asphaltene precipitation but they disperse precipitated asphaltenes to avoid either asphaltene deposits or aggregation (Eigner, 2016).

Several researches agreed that asphaltenes particles are kept under colloidal suspension in crude oils through interactions between natural surfactant groups in resins compounds and asphaltene superficial charges (Junior *et al*., 2006; Mirzayi *et al*., 2012; Karambeig *et al*., 2016). When a precipitant (e.g. n-heptane) is added to the fluid, resins are dissolved in the oil, creating active areas of asphaltene particles, which permit the particles agglomeration and then precipitation. Thereby, asphaltene inhibitors are charged with groups that aim to mimic resins preventing agglomeration of asphaltene particles and shifting the asphaltene onset pressure (Oilfield Wiki, 2016).

With regards to the estimation of chemical solvents for asphaltene precipitation, several remedial procedures such as cleaning with chemical solvents, washing with hot solvents or water steam and application of inhibitors or dispersants have been proposed to remove asphaltene deposition throughout the oilfields. Clearly, solvent treatment is considered a great solution; an example is the report of the effective application of aromatic compounds such as toluene, Xylene, benzene and chlorate to dissolve asphaltenic deposits since asphaltene solubility increase as long as aromatic content increase. Nevertheless, these solvents are no long being used because they are extremely harmful for the health and environment (Junior *et al*., 2006; Elochukwu *et al*., 2014; Larichev *et al*., 2016). Besides, these procedures for deposits removal can lead pauses in the production. Applying chemical substances which can successfully stabilize or solubilize asphaltene before its precipitation is an excellent way of either prevent or mitigate asphaltic deposits formation. Moreover, it can reduce economical loss and provide easeful application. (Junior *et al*., 2006).

Junior *et al*. (2006), had evaluated the inhibition of asphaltene precipitation in Brazilian crude oil through addition of a new number of chemical amphiphiles (ethoxylated phenols, vegetable oils and organic acids). The dissolution process of these additives was verified in two aspheltenic deposits mixed with aliphatic solvents. Dodecylbenzenesulfonic acid had displayed a phenomenal solubilization effect somewhat proved the utmost importance of acid-base interactions between asphaltene and additives. Furthermore, the results divulged distinct mechanisms for asphaltene dispersion in aliphatic solvents as well as inhibition of asphaltene precipitation.

According to the research, the influence of ionic liquids on inhibition of asphaltene precipitation had been investigated too. Researches explained that polar compounds of crude oils (e.g. asphaltene) would diffuse in ionic liquids and consequently reduce the crude viscosity and asphaltene content as well, thereby enhancing oil recovery (Nares *et al*., 2007 & Hezave *et al*., 2013).

Karambeigi *et al*. (2015) developed an experimental evaluation of 6 different asphaltene inhibitors (IR95, benzoic acid, salicylic acid, phenanthrene, and phthalic acid) in order to understand the impacts these substances could bring on the reduction of asphaltene precipitation, onset shifting and asphaltene deposition under reservoir conditions. The results proved that salicylic acid provides better efficiency to stabilize asphaltenes rather than other non-commercial inhibitors with 34% asphaltene precipitation reduction while IR95, on the other hand, owing to high capability to be absorbed on the porous media leads to the reoccurrence of asphaltene precipitation.

Recently, the influence of several organic solvents on the size and shape of asphaltene particles was investigated by Larichev *at al*., (2016). In their results, they had shown that compounds as decalin, dimethylformamide, dimethylsulfoxide, nitrobenzene, aniline, cyclohexanol, monoethanolamine, triethanolamine, 1-methylnaphtalene, and dichloroethane when added into crude oil lead to asphaltene disaggregation because of their physic-chemical properties.

The effectiveness of chemical inhibitors is still a matter for a debate, however if it works, its efficiency can be roughly 50-70% from field to field (Eigner, 2016), since each inhibitor performance are oil specific. A chemical can be efficient on one type of crude and do not be efficient on other oils.

Therefore, many researchers’ groups have made efforts to either investigate or understand the performance of several chemical inhibitors for enhancing of asphaltene stability/solubilization in different crude oils so that it can mitigate asphaltene precipitation phenomenon (Oilfield Wiki, 2016).

In the present research, the performance of two solvents (salicylic acid and *iso*- phthalic acid, see table 5 for more information) will be evaluated in crude oil samples of one of the South African oilfields and their results will be discussed on the chapter IV.

CHAPTER III: Methodology

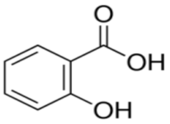
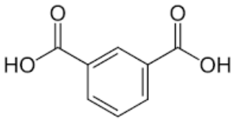
3.1. Introduction

Asphaltenes precipitation during crude oil transportation from production site to refining processes is controlled by parameters such as temperature, pressure and oil composition.

Firstly, in this project methods for asphaltene separation from a dead crude oil were applied in order to characterise and identify asphaltene content into the fluid sample. According to the presence or absence of gas (mainly methane) crude oil can be classified as dead or live. Dead oil is considered oil at sufficiently low pressure which there is no presence of dissolved gas or either residue that has lost its volatility (e.g. heavy oil, tar and bitumen). Basically, when crude oil is obtained at the surface conditions it goes through one or more separators in which the solution gas (C_1 and some C_2) will be released from the crude oil. The other lighter components as C_3, C_4 and some C_5 can be stripped off from the crude through NGL recovery methods. Therefore, after all these processes, the oil transported through pipelines or tankers to terminals for refining or for further uses is referred as dead crude oil. On the other hand, live oil is considered oil produced in reservoir conditions which contain dissolved gas in solution that may be separated from the oil at surface conditions or atmospheric pressure (e.g. normal black oil and near critical oil) (De Andrade & Rajagopal, 2017; Oilfield, 2017)

Secondly, the asphaltene precipitation onset time was evaluated at different temperatures through addition of a precipitant (n-heptane) and then the asphaltene particles aggregation was confirmed with a microscope. This step provided a platform for better understanding of asphaltenes behaviour during its transportation when changes in temperature and fluid composition occur. From the critical temperature range that was determined from the previous steps, the performance of salicylic acid and *iso*-phthalic acid (see their properties on the table 5) on asphaltene precipitation onset time was analysed at different concentrations and lastly the asphaltene reduction percentage in the crude oil was investigated based on different techniques.

Table 5: Inhibitors chemical properties. S.A. MSDS*& I.A. MSDS**

Name	***Molecular formula***	***Molecular weight (g/mole)***	***Density*** (g/cm^3) ***at 15.56ºC***	***Chemical structure***
Salicylic acid*	$C_7H_6O_3$	138.12	1.85	
Iso- phthalic acid**	$C_8H_6O_4$	166.13	1.53	

a) Materials and equipments

Table 6: Material and/or equipment used during the experiments.

Material/Equipment	**Comments**
Crude oil samples	Supplied by Sasol
Salicylic acid (powder)	Provided by RADCHEM
Iso-phthalic acid (powder)	Provided by Lab BDH
n-heptane	Provided by Merck, 99%
Toluene, Ethanol, Methanol	Provided by Fluka Analytical
Glass flask	10, 50, 500mL
Evaporating vessel	
Graduated cylinders	10, 50, 100mL
Stirring rods	150mm by 3mm diameter
Funnel filter assembly	

Filter paper (125mm diameter)	Watman grade 42
Analytical balance	EXPLORER Pro
Oven	Quincy lab
Mixer-Heater	Lab-Line Multi-Blok
Mass Spectrometry	LECO PEGASUS 4D
Optical microscope	OLYMPUS SC50
Centrifuge	Thermofisher

b) Sample preparation

- ***Solvents preparation***

Solution of 2.5%, 5.0% and 10% of salicylic acid and *iso*- phthalic acid were made based on 0.985g, 1.97g and 3.94g respectively of solvent powder dissolved into 50mL of ethanol. All solutions were shaken in a mixer until the powder became completely dissolved. Then the solutions were kept in a safe place at ambient temperature in order to avoid any kind of incident.

- ***Crude oil preparation***

A sample of 10mL of dead crude oil was withdrawn into a glass flask and centrifuged at 9000rpm for 3h to ensure removal of water, sand and other particles. Then different volumes of crude oil were withdrawn into vials and taken for SARA analysis based on *IP 143* Standard test and ASTM D2007 procedures, and determination of asphaltene precipitation onset.

3.2. Quantification of asphaltene precipitation

Quantification of asphaltene into crude oil is usually made through determination of asphaltene content. It is described as the percentage weight of insoluble compounds in a precipitant solvent (mainly *n*-heptane), empirical data from several stability studies have revealed that crude oil with asphaltene content numbers of 7 or less frequently contain unstable asphaltene while those with values higher than 12 have stable asphaltene. Oils which show values from 8 to 12, their stability is uncertain, since the asphaltene could be stable, unstable or either of minimal stability (Asomaning, 2003).

under specific test conditions. The establishment of asphaltene content is part of crude oil risk assessment used in its commercialization. In addition, asphaltene content affects the stability, compatibility and crude oil processability during its production and refining (Colaiocco & Farrera, n.d.; Zhang, *et al*., 2007).

Nevertheless, the presence of asphaltene does not mean asphaltenic oilfield problem in the future. Heavy oils with high asphaltene content (values above 12) are generally stable during production and do not cause well blocking while light oils with low amounts of asphaltene (values below 7) have a propensity to precipitate and cause severe asphaltenic problems (Zhang, *et al*., 2007).

In this work, for measuring precipitated asphaltenes, *IP/143 standard method* was applied as shown in the block diagram in the Appendix A.

After asphaltene extraction from a volume of 2.30mL of crude oil, the weight of dried asphaltene was calculated by subtracting the weight of dried weighing glass flask and all filter papers used during the filtration from the total weight of asphaltene before drying. The process to obtain mass of dried asphaltene was repeated three times in order to obtain the SD between the three measurements based on equation 1. The results can be seen on table 7.

Equation 1

$$\mathrm{SD} = \sqrt{\frac{\sum(x-\mu)2}{n}}$$

Where ∑ means sum of, **x** is a value in the data set, **μ** is the mean of the data set and **n** is the number of scores in sample.

After having the average of the masses of dried asphaltene, asphaltene content was calculated through equation 2.

Equation 2

$$\text{Asphaltene content} = \frac{\text{Weight of dried asphaltene (g)}}{\text{Crude oil volume (mL)}} * 100$$

3.3. Evaluation of asphaltene stability in the crude oil samples

Asphaltene stability was determined through CII equation. However, to calculate CII, SARA analysis based on ASTM D2007 procedure method was used. After extracting asphaltene from the crude samples through *IP/143* procedures, the new sample called maltenes (oil without asphaltene) was then further separated by passing the solution through a chromatography column packed with silica. From this step, the three fractions (aromatics, saturates and resins) were sequentially flushed and removed using different solvents (see figure 32, Appendix B), therefore separating crude oil into four fractions, namely asphaltene, aromatics, saturates as shown by figure 9.

Figure 9: Fractionation of saturates, aromatics, resins and asphaltenes (Zhang *et al.*, 2007)

As discussed on the previous chapter (section about asphaltene stability), CII is the most accurate measurement used to determine asphaltene stability in the crude samples. It is described as the sum of asphaltenes and saturates (asphaltenes' flocculants) divided by the sum of resins and aromatics (asphaltenes peptizers) as shown in the equation 3:

Equation 3

$$\text{CII} = \frac{\text{Asphaltenes (A)} + \text{Saturates (S)}}{\text{Resins (R)} + \text{Aromatics (A)}}$$

Empirical analysis has demonstrated that crude oil with CII equal or higher than 0.9, crude oil presents unstable asphaltene; between 0.7 and 0.9, asphaltene instability is unclear and below 0.7 presents stable asphaltenes.

3.4. Detection of asphaltene precipitation onset

- **Room temperature experimental procedure (20ºC)**

In this study, a microscope was used to investigate asphaltene precipitation onset in crude oil samples. Firstly, 10g of crude oil sample was pre-homogenized manually by shaking the sample for 5min. Then, 0.5g of oil was measured and observed in the microscope to make sure there is no presence of any visible particles. Then, 2mL of *n*-heptane was added in to the vial and the sample was shaken in a mixer for 10min. The sample was left to rest at room temperature for 20min. Secondly, the sample was observed in different times until the appearance of visible asphaltene aggregated particles as show figure 10.

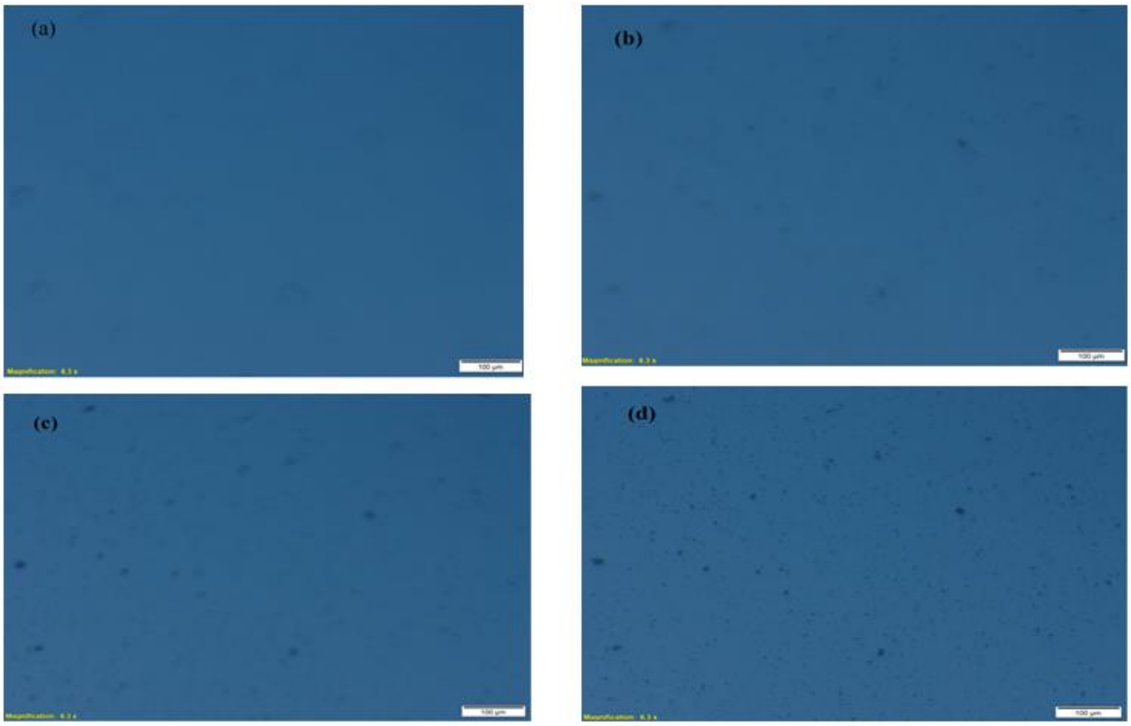


Figure 10: Asphaltene aggregation stages in oil + n-C7 sample as a function of time and n-heptane addition. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 160min; (c) 3.5ml added n-C_7- 192min; (d) 4.5mL added n-C_7- 231min.

Then, a volume of 2mL of solutions containing 2.5%, 5.0% and 10% of chemical inhibitors were added into 0.5g of oil samples without *n*-heptane and centrifuged for 10min, to ensure total solvent dilution. The samples were further gradually mixed by amount of n-heptane until the asphaltene particles were observed on the microscope. All images and time of particles growth can be seen from figure 11 to 16.

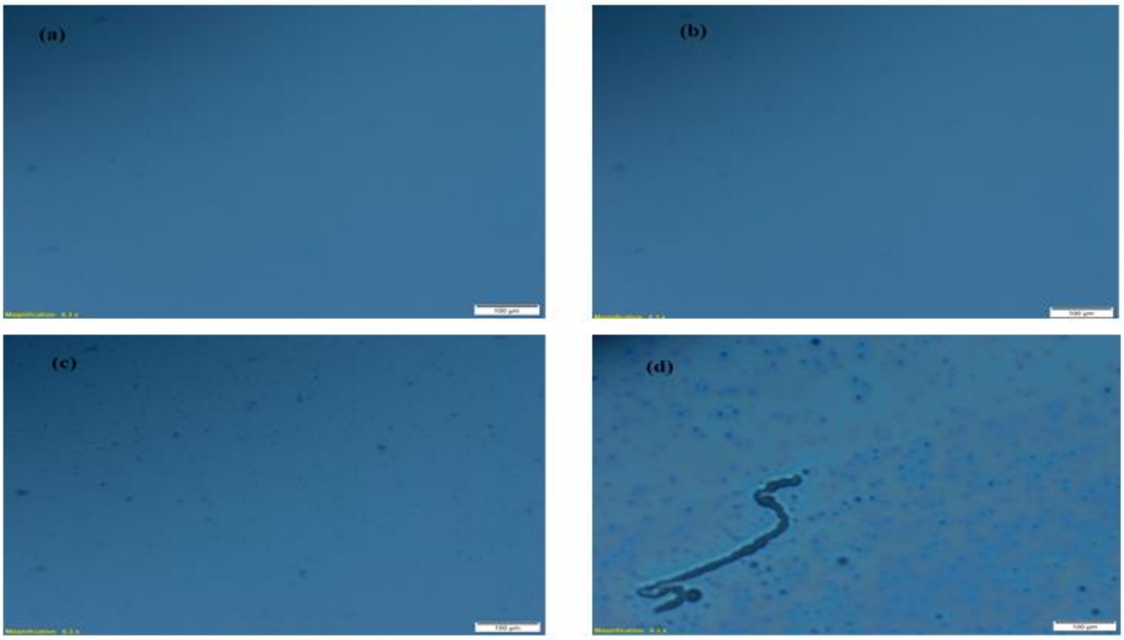


Figure 11: Asphaltene aggregation stages in oil + 2.5% of S.A. + n-C_7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 226min; (c) 4.5ml added n-C_7- 294min; (d) 4.7mL added n-C_7- 309min.

Figure 12: Asphaltene aggregation stages in oil + 5% of S.A. + n-C7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 301min; (c) 6.3ml added n-C_7- 385min; (d) 7.7mL added n-C_7- 430min.

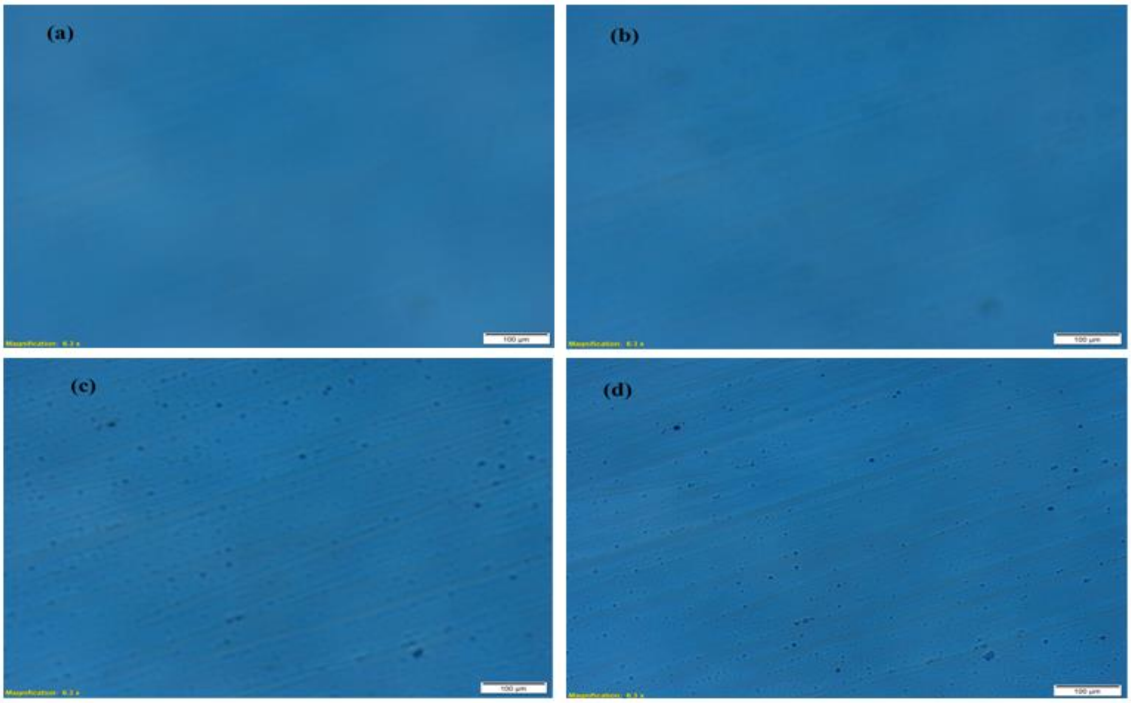


Figure 13: Asphaltene aggregation stages in oil + 10% of S.A. + n-C7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 436min; (c) 7.5ml added n-C_7- 538min; (d) 8.4mL added n-C_7- 679min.

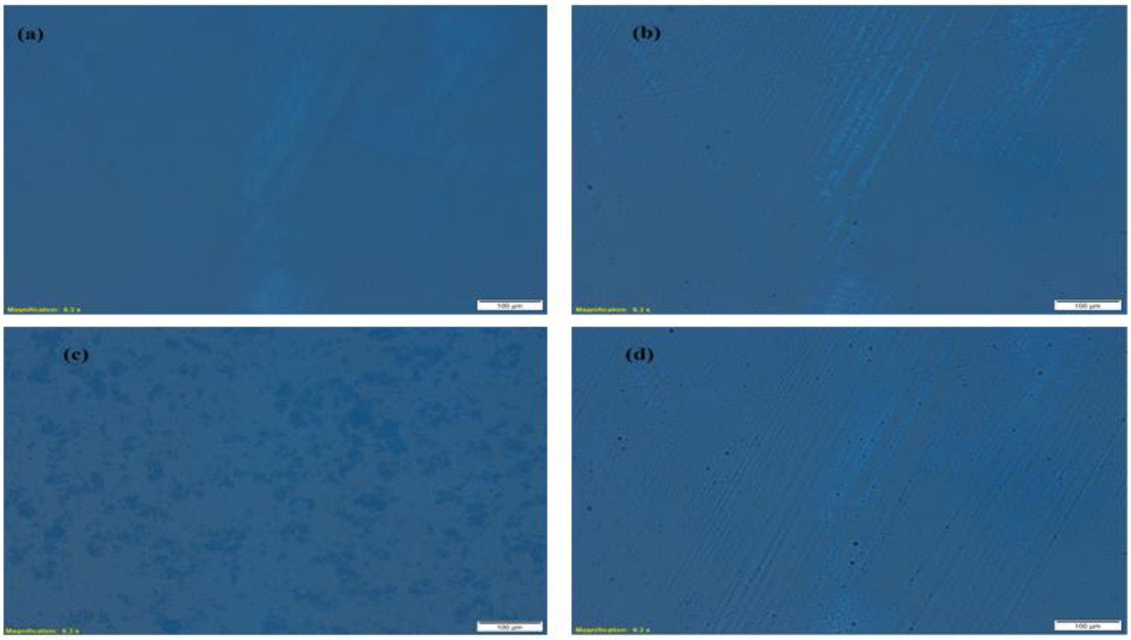


Figure 14: asphaltene aggregation stages in oil + 2.5% of I.A. + n-C7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C7- 413min; (c) 7.0ml added n-C_7- 522min; (d) 7.9mL added n-C_7- 633min.

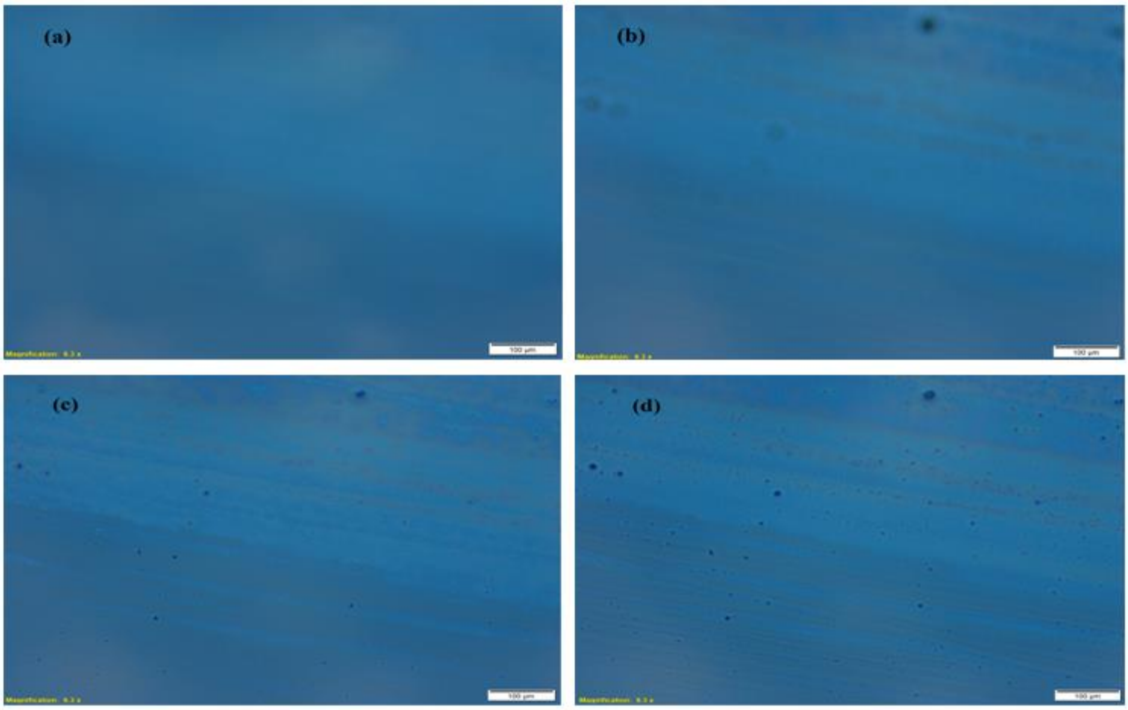


Figure 15: Asphaltene aggregation stages in oil + 5% of I.A. + n-C7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 121min; (c) 2.7ml added n-C_7- 255min; (d) 3.3mL added n-C_7- 330min.

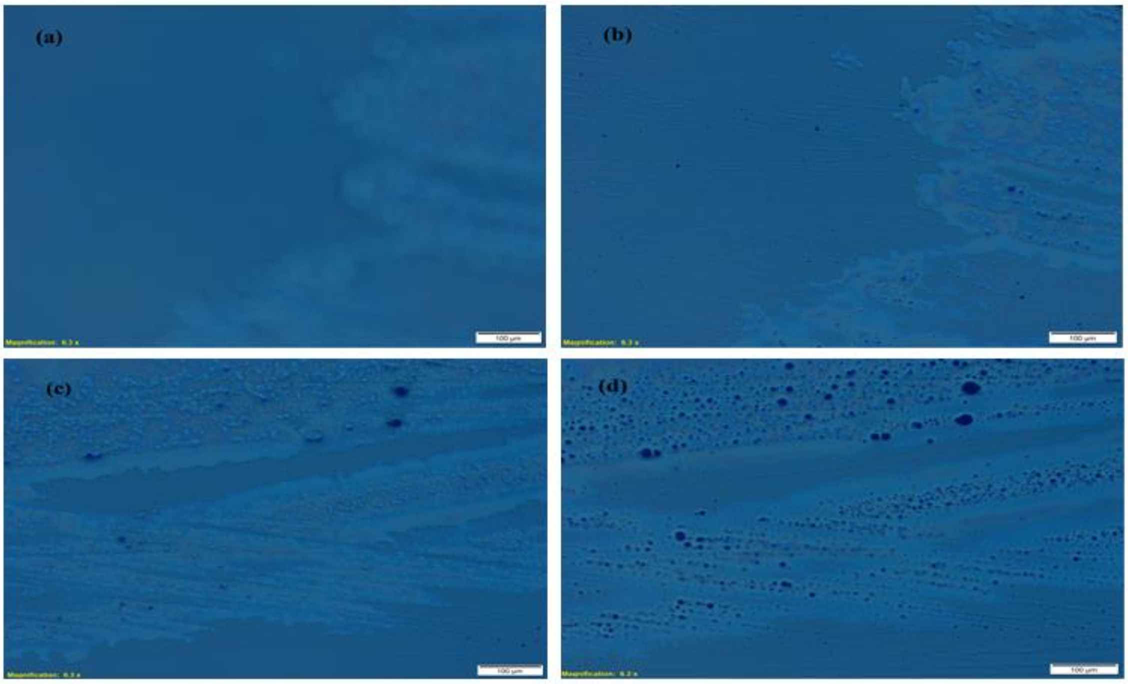


Figure 16: Asphaltene aggregation stages in oil + 10% of I.A. + n-C7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 91min; (c) 2.5ml added n-C_7- 133min; (d) 2.7mL added n-C_7- 209min.

- **High temperature experimental procedure (50°C)**

Asphaltene precipitation onset time in high temperature also was investigated. The present methodology used was a modification of the methodology proposed by Maqbool *et al*. (2010), which was conducted in a temperature controlled water-bath where oil samples are kept stirred all the time.

In the methodology of this research, oil samples without and with inhibitors were kept in water-bath for 12 hours. A thermocouple was introduced in the water, just to help controlling the desired temperature. The bath being heated through a hot plate was closed with aluminum paper foil to avoid heat losses.

The crude oil samples were prepared and observed into the microscope following the abovementioned steps. All samples were closed during the entire analysis to prevent precipitant and solvent losses as well as they were observed in the microscope until the first nano- aggregate particle as show from figure 17 to 23.

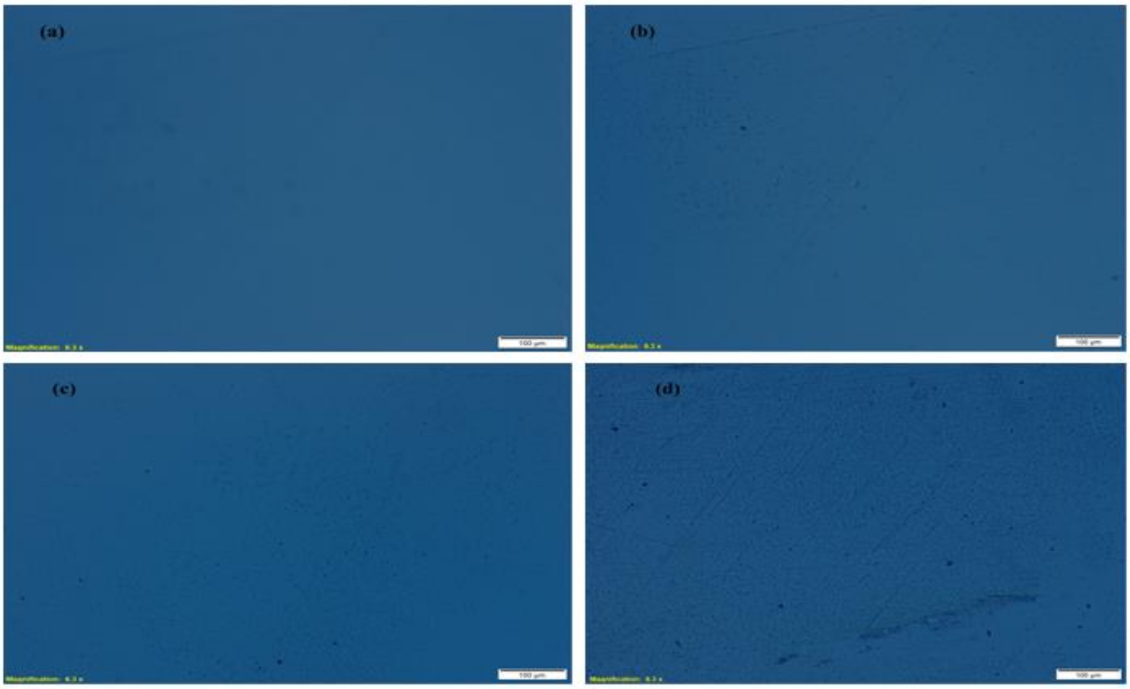


Figure 17: Asphaltene aggregation stages in oil + n-C_7 sample as a function of time and n-heptane addition. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 152min; (c) 3.2ml added n-C_7- 177min; (d) 4.3mL added n-C_7- 196min.

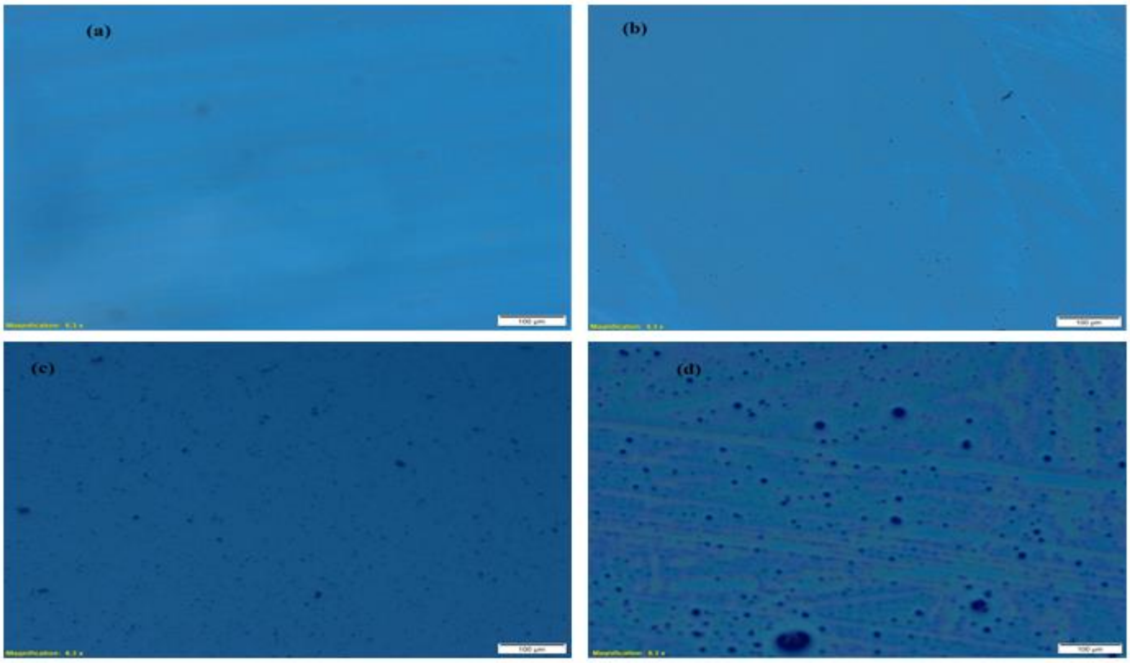


Figure 18: asphaltene aggregation stages in oil + 2.5% of S.A. + n-C_7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 200min; (c) 2.5ml added n-C_7- 259min; (d) 3.5mL added n-C_7- 303min.

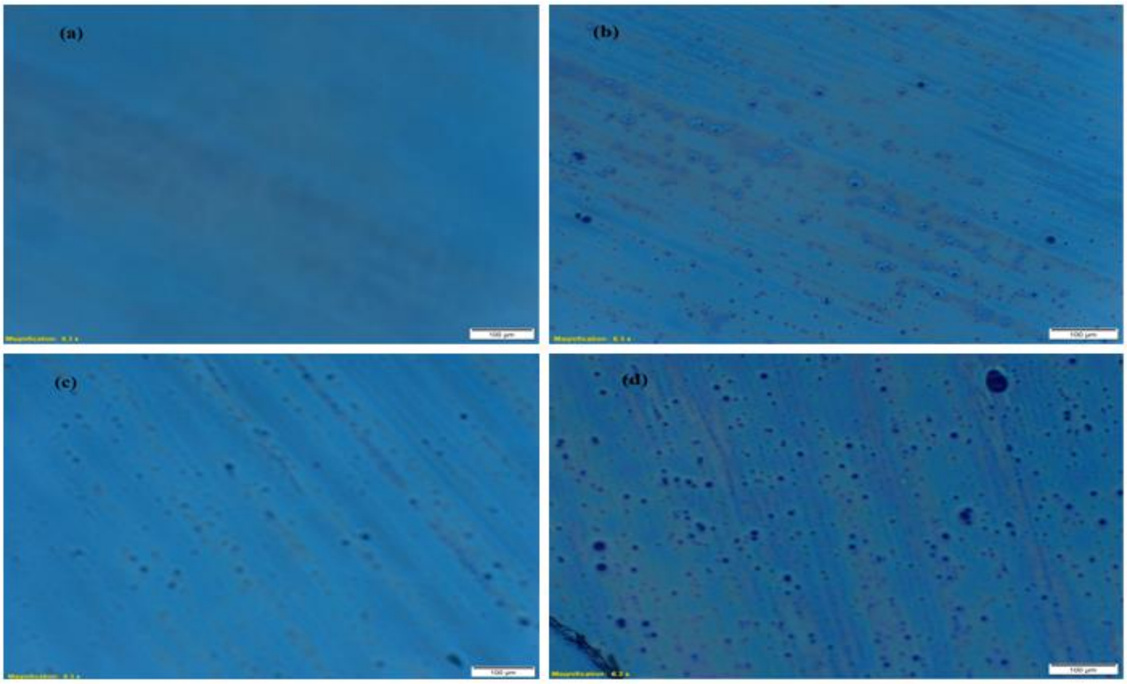


Figure 19: Asphaltene aggregation stages in oil + 5% of S.A. + n-C7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 186min; (c) 3.3ml added n-C_7- 217min; (d) 3.6mL added n-C_7- 298min.

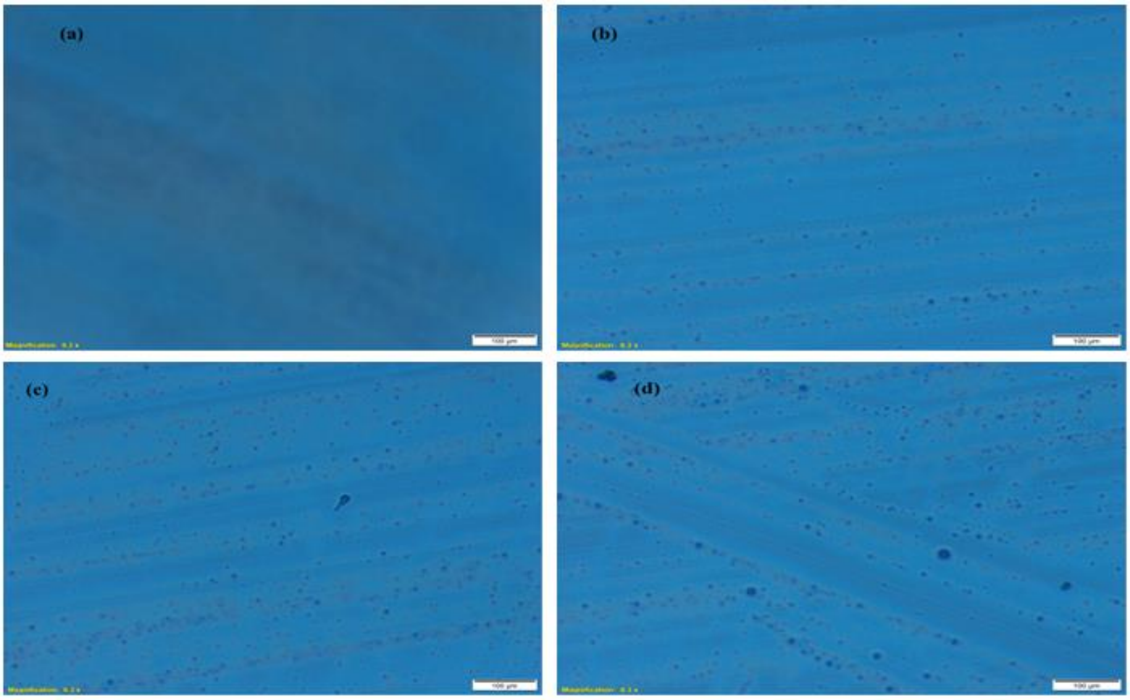


Figure 20: Asphaltene aggregation stages in oil + 10% of S.A. + n-C_7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 372min; (c) 2.5ml added n-C_7- 420min; (d) 3.9mL added n-C_7- 505min.

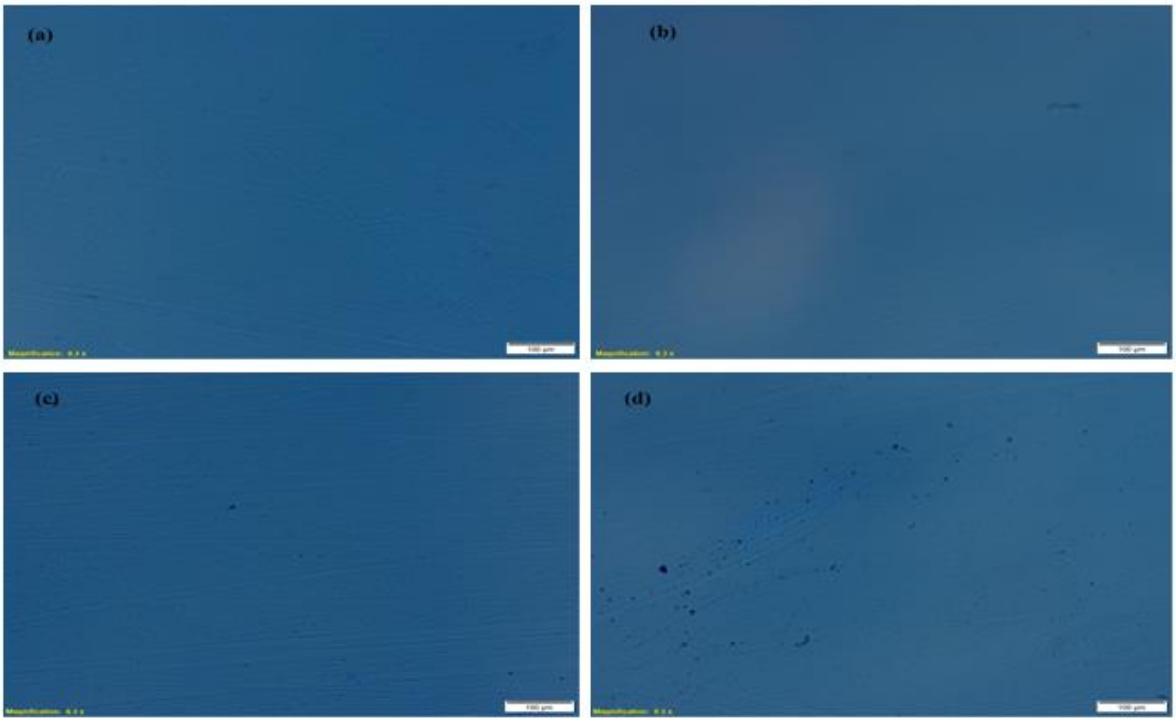


Figure 21: Asphaltene aggregation stages in oil + 2.5% of I.A. + n-C_7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 475min; (c) 6.3ml added n-C_7- 580min; (d) 7.6mL added n-C_7- 679min.

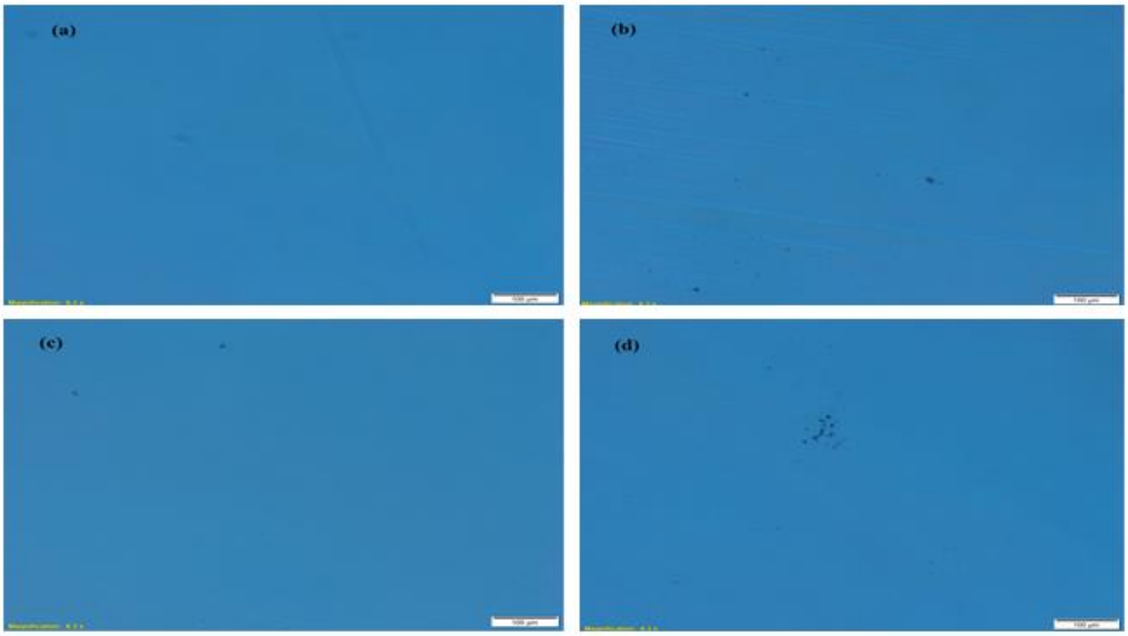


Figure 22: Asphaltene aggregation stages in oil + 5% of I.A. + n-C_7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 498min; (c) 5.8ml added n-C_7- 600min; (d) 8.1mL added n-C_7- 696min.

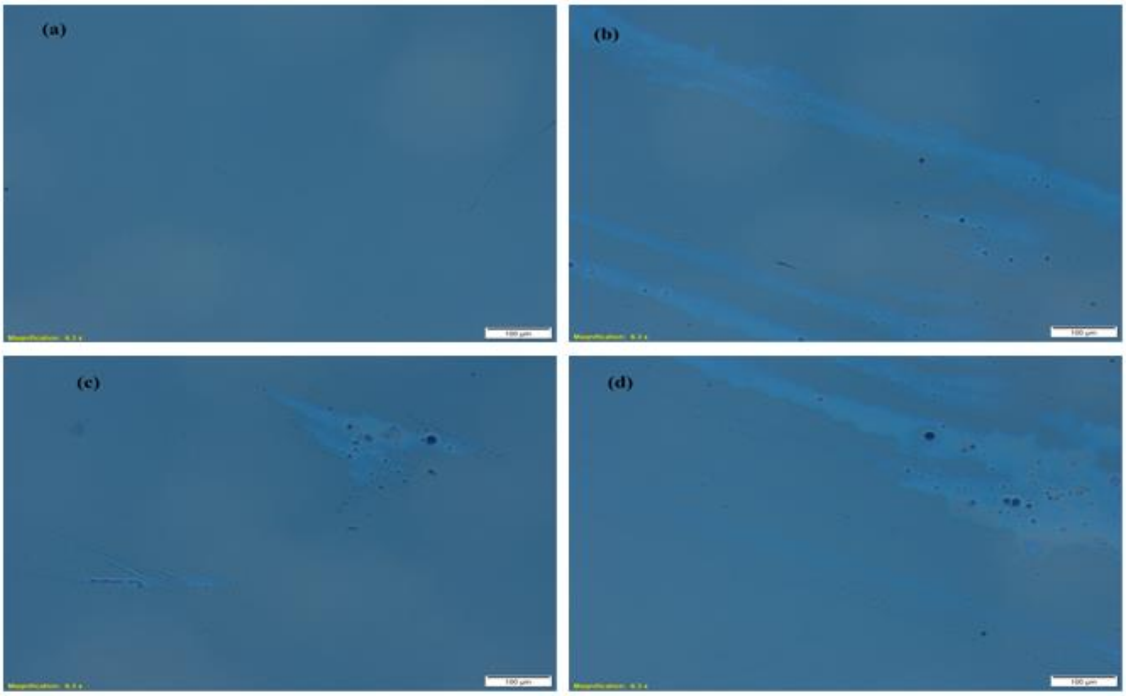


Figure 23: Asphaltene aggregation stages in oil + 10% of I.A. + n-C_7 sample. (a) 0mL added n-C_7- 0min; (b) 2ml added n-C_7- 542min; (c) 6.1ml added n-C_7- 631min; (d) 8.5mL added n-C_7- 720min.

3.5. Solvents/ precipitant mixtures assessment

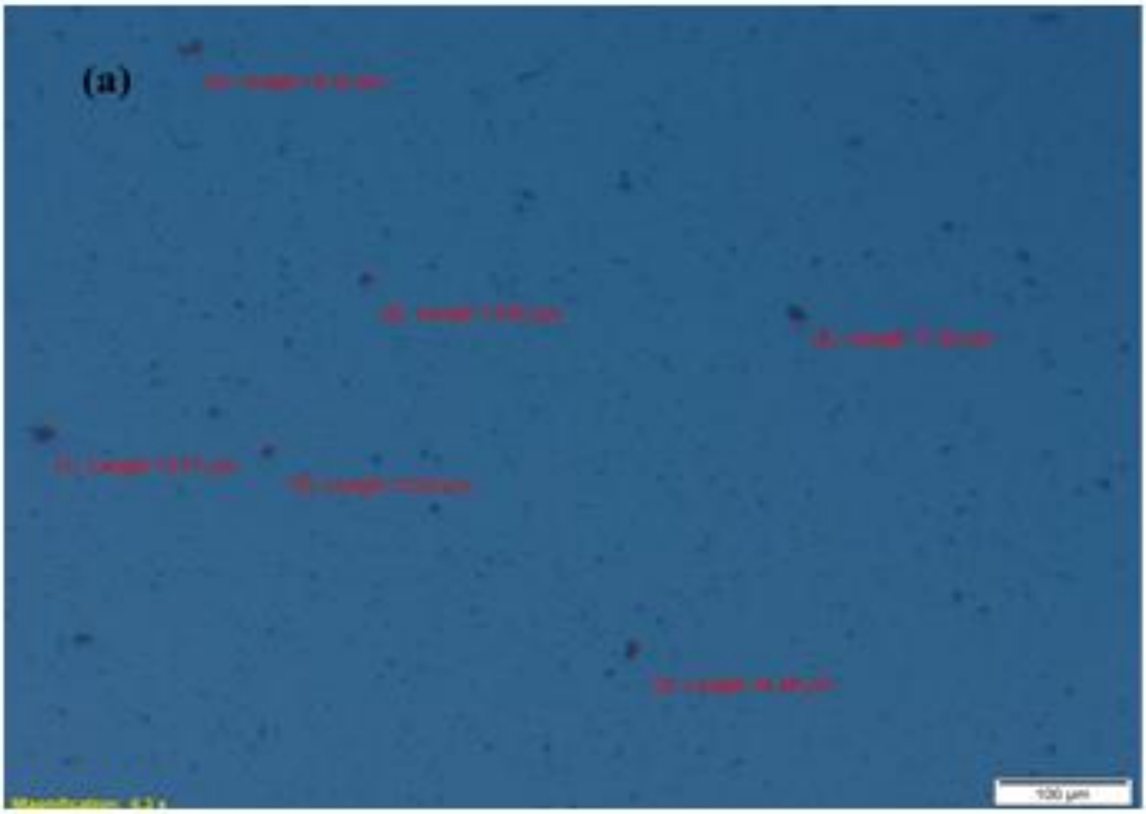
In this research, the selection of the chemical inhibitors was based on three factors:

(i) *Being environmental friendly*: According to MSDS of salicylic acid and Iso-phthalic acid, both products do not demonstrate relevant safety and environmental issues. Both are classified as non-corrosive, S.A. shows low flammability (1.1%) while I.A. is inflammable. There is no case identified of eco-toxicity problems caused by S.A and any hazardous short-term degradation products are expected. On balance, for I.A. no case of toxicity problems is known and it is 85-90% readily biodegradable. Both of them can be stored in light resistant containers and do not require any special waste disposal consideration.

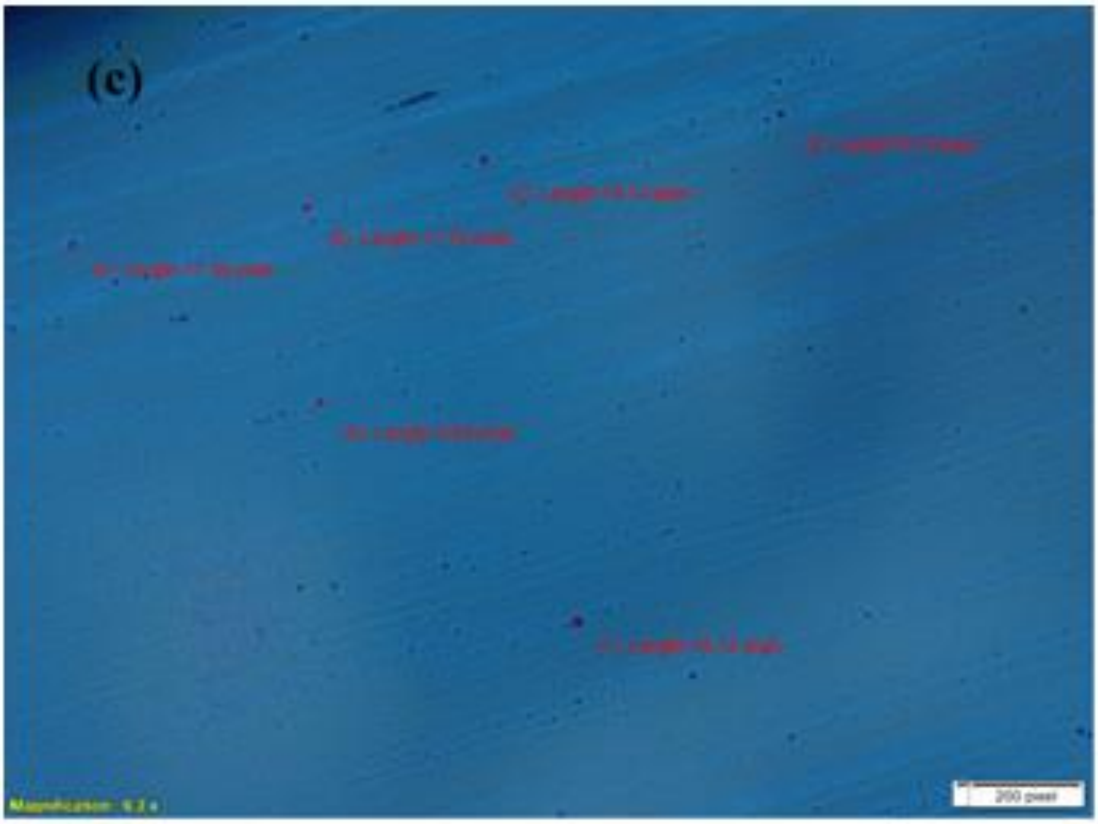
(ii) *Commercial availability*: Both chemical products were commercially available in the Chemistry store at Chemistry department- University of The Witwatersrand.

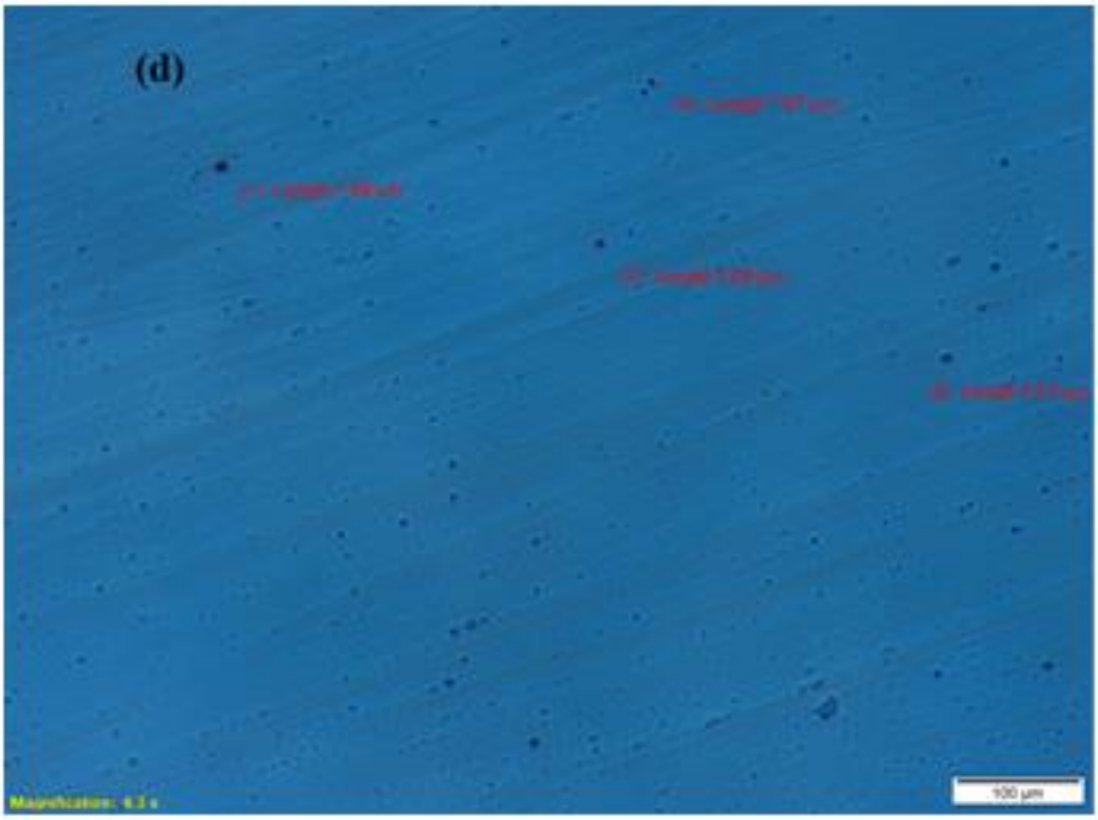
(iii) *Compatibility with oil fractions*: as mentioned in section 2 (solvents inhibitors) few studies of successful application of S.A. in different oilfields have already been reported. However, these studies have not assessed S.A. effectiveness at high temperatures, and that's the reason why its study was extended in this research. In case of I.A, there is no any case study available yet, Karambeigi *et al.*, 2015 had investigated the performance of phthalic acid (isomer of iso-phthalic acid) among other 5 solvents, however phthalic acid to a certain extent, demonstrated the poorest effectiveness when compared to the other 5. Therefore, in this research assessment of phthalic acid isomer was proposed.

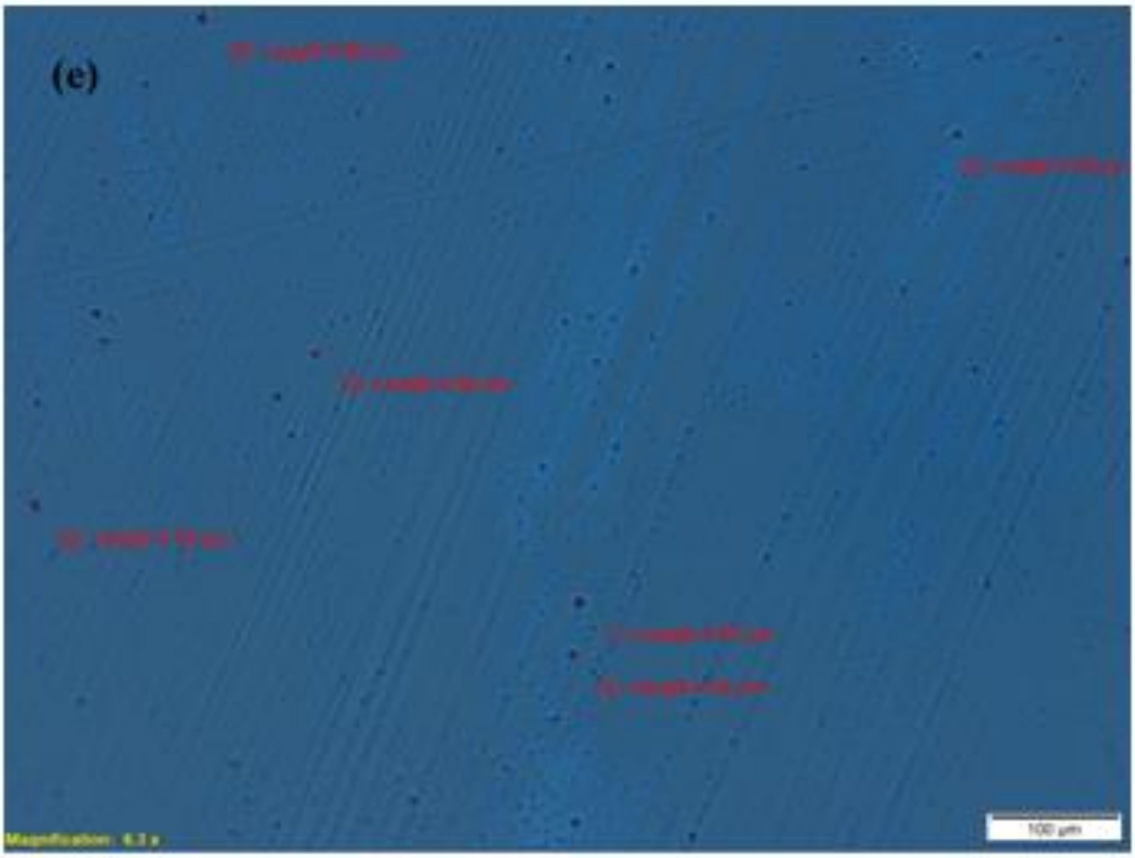
The performance of the inhibitors in retarding asphaltene precipitation phenomenon was observed based on microscope images that show asphaltene aggregation stages as function of time and n-C_7 addition at 20ºC (figure 24) and 50ºC (figure 25) as well as determined through comparison of the particles sizes of precipitated asphaltene when reached the precipitation onset point in samples with and without solvents.

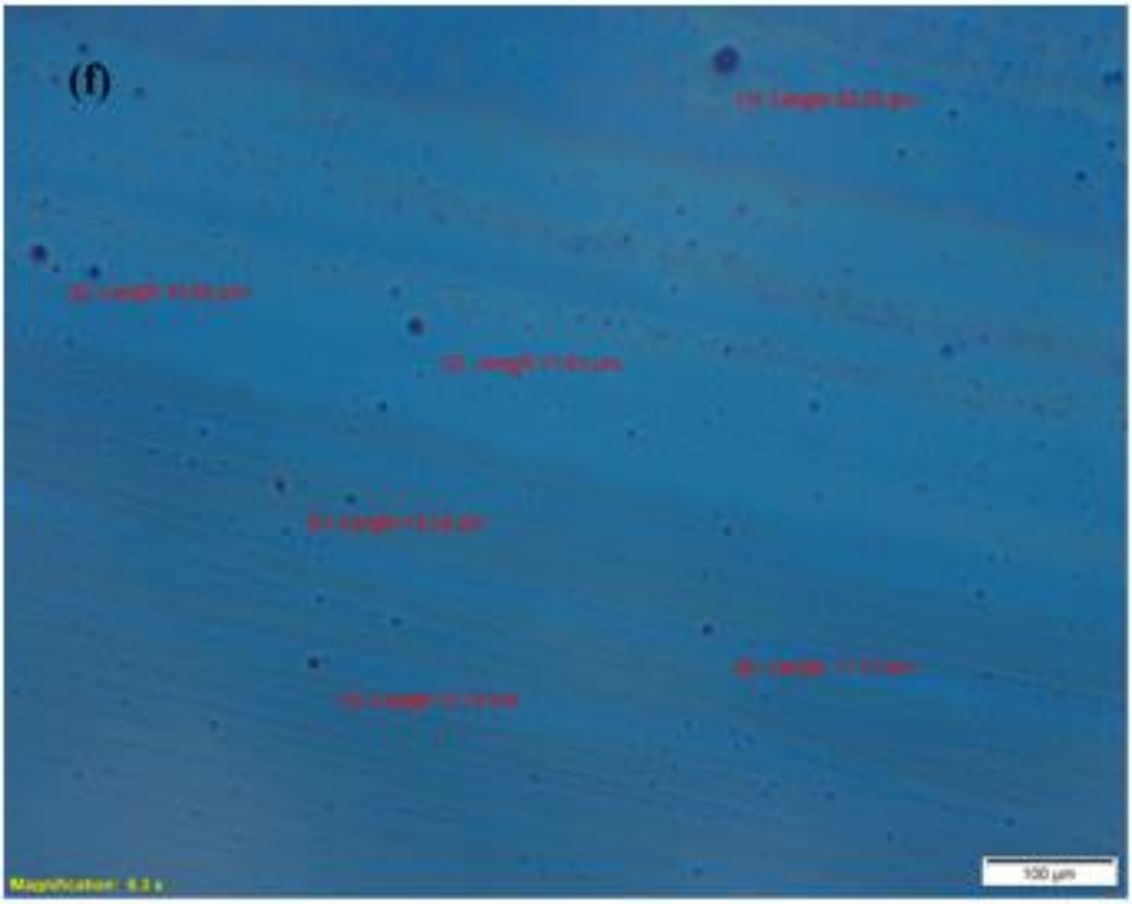

(a)
100 µm


(b)
100 µm


(c)
Magnification: 6.3 x
200 pixel


(d)
Magnification: 6.3 x
100 µm


(e)
Magnification: 6.3 x
100 µm


(f)
Magnification: 6.3 x
100 µm

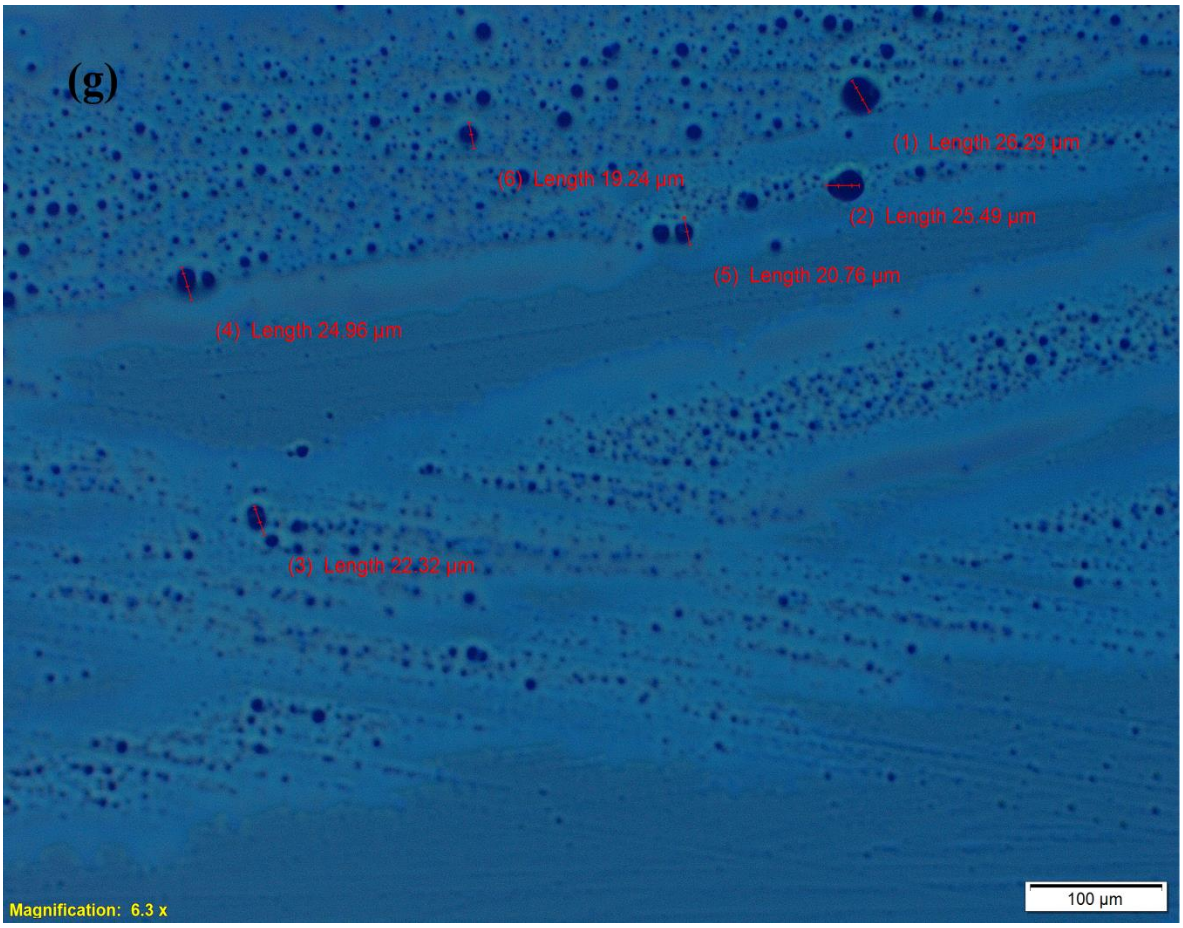
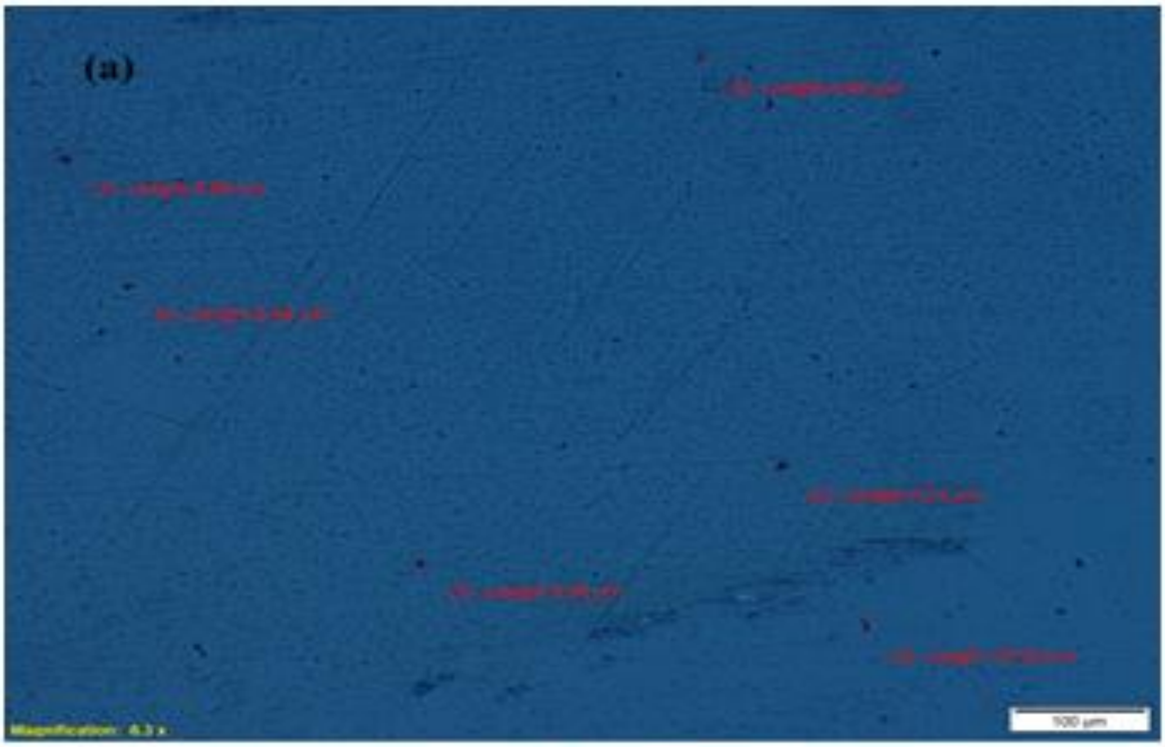
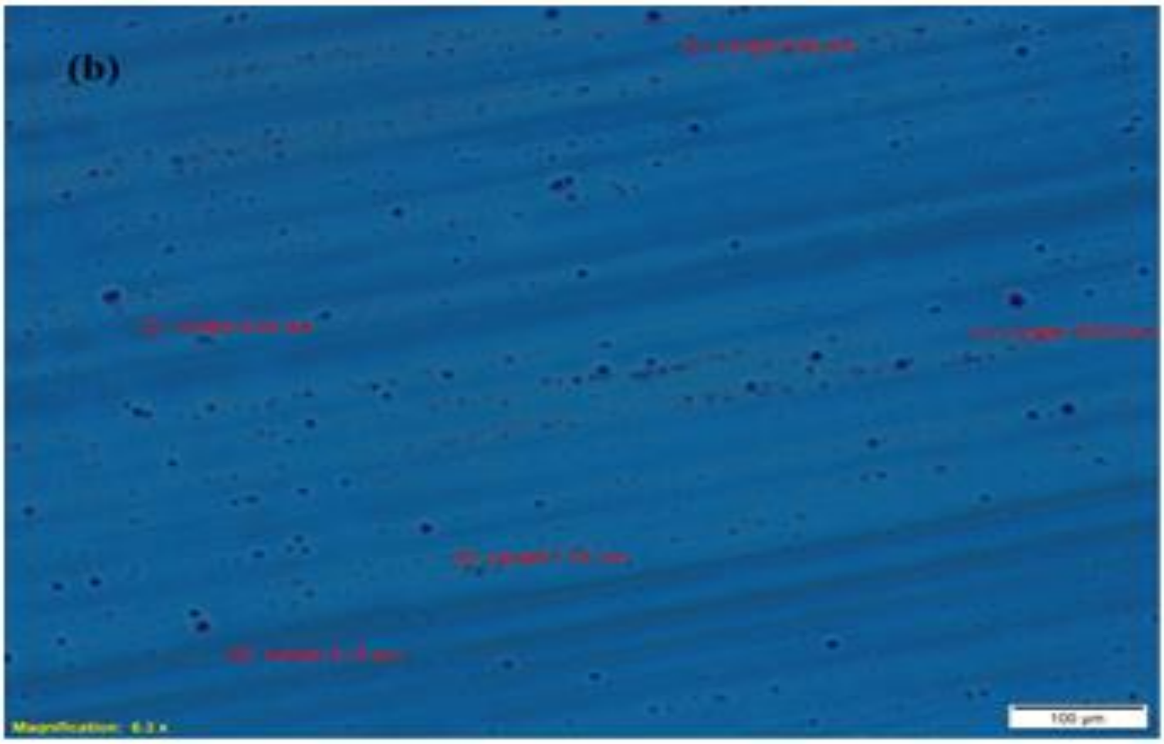
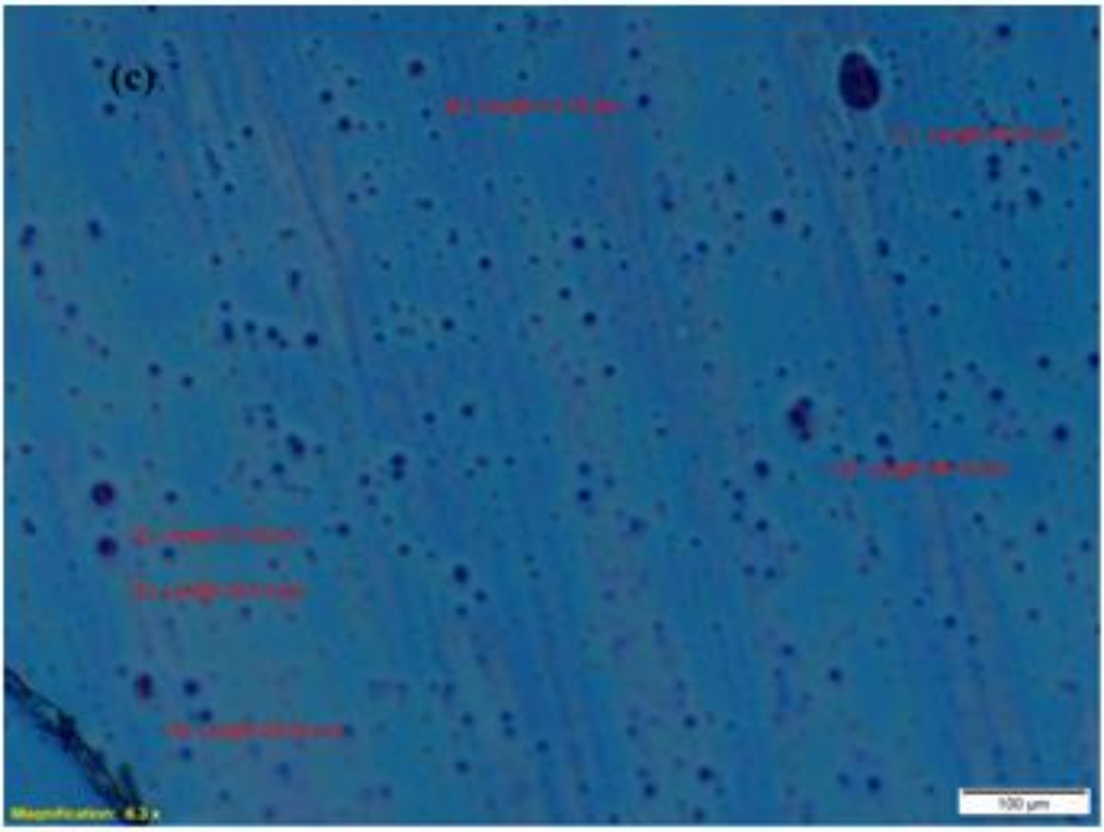
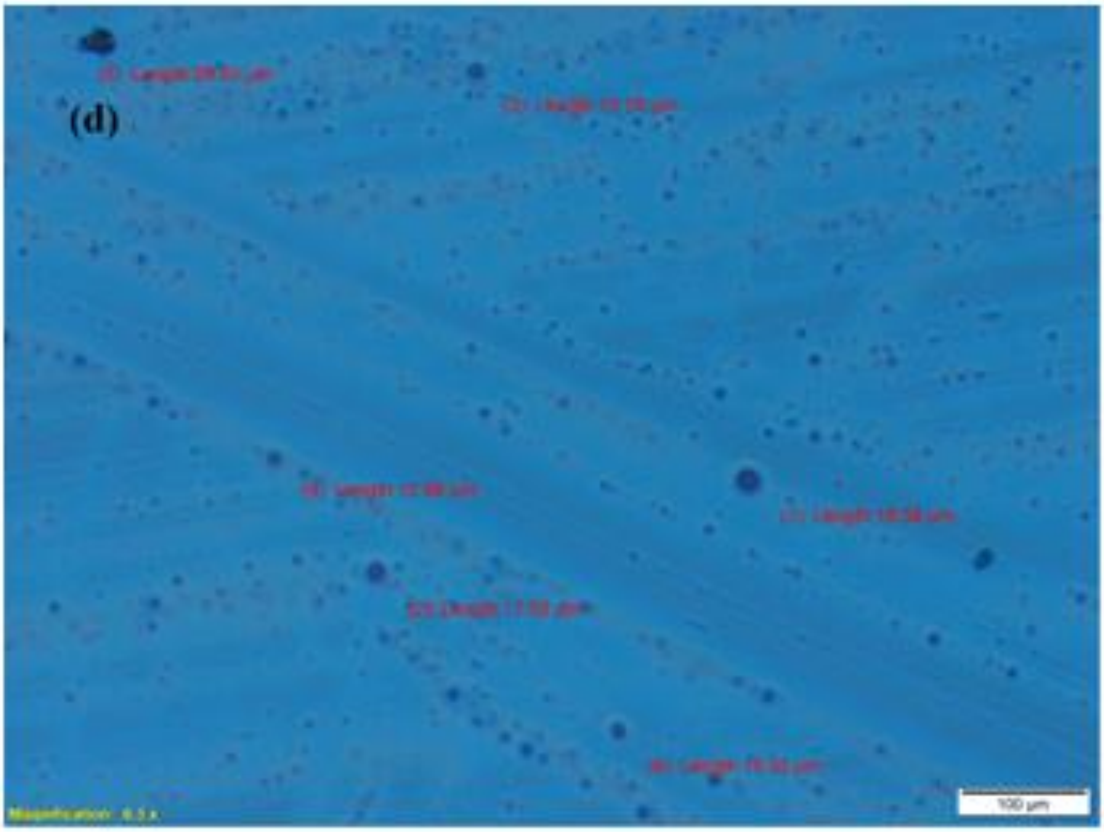


Figure 24: Precipitated asphaltenes in different samples at 20^{o}C. (a) crude oil + n-C_7; (b) crude oil+ S.A. 2.5% + n-C_7; (c) crude oil + S.A. 5.0% + n-C_7; (d) crude oil + S.A. 10% + n-C_7; (e) crude oil + I.A. 2.5% + n-C_7; (f) crude oil + I.A. 5.0% + n-C_7; (g) crude oil + I.A. 10% + n-C_7.

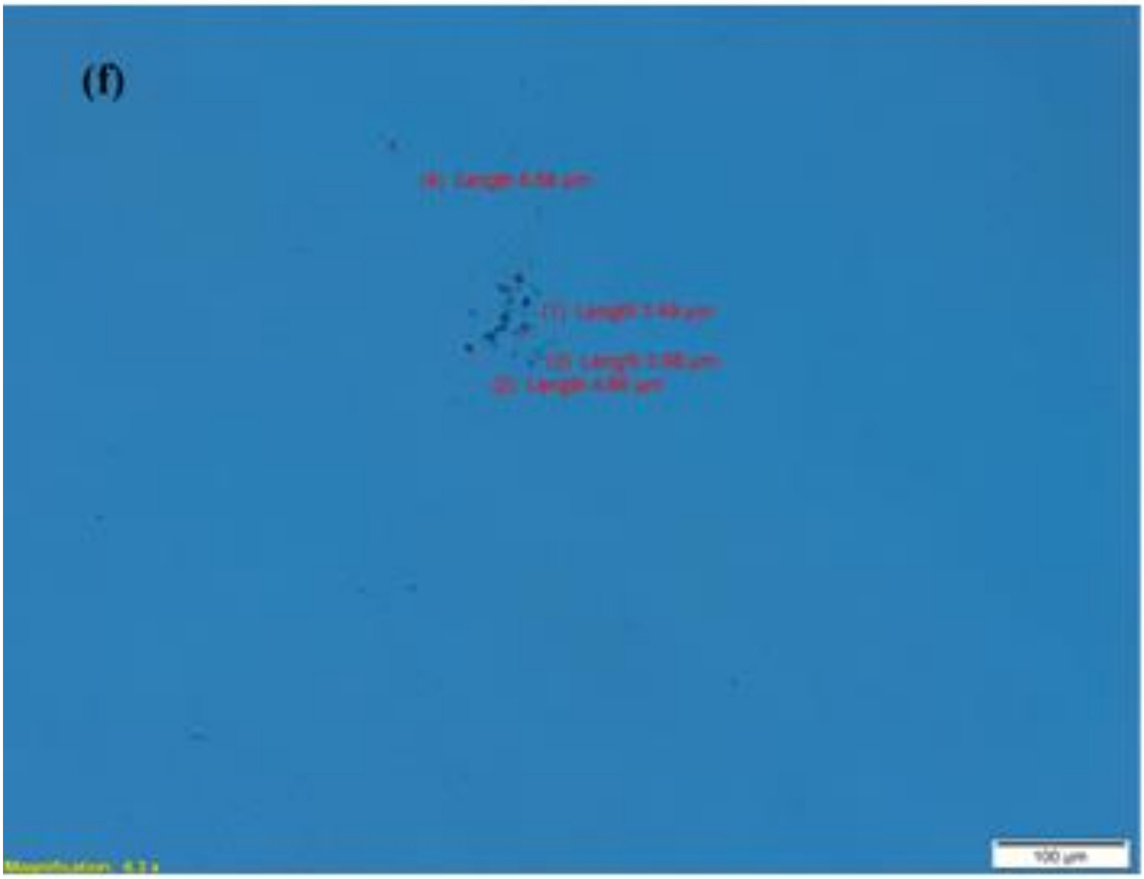

(a)
Magnification: 6.3 x
100 µm


(b)
Magnification: 6.3 x
100 µm


(c)
Magnification: 6.3 x
100 µm


(d)
Magnification: 6.3 x
100 µm


(e)
Magnification: 6.3 x
100 µm


(f)
Magnification: 6.3 x
100 µm

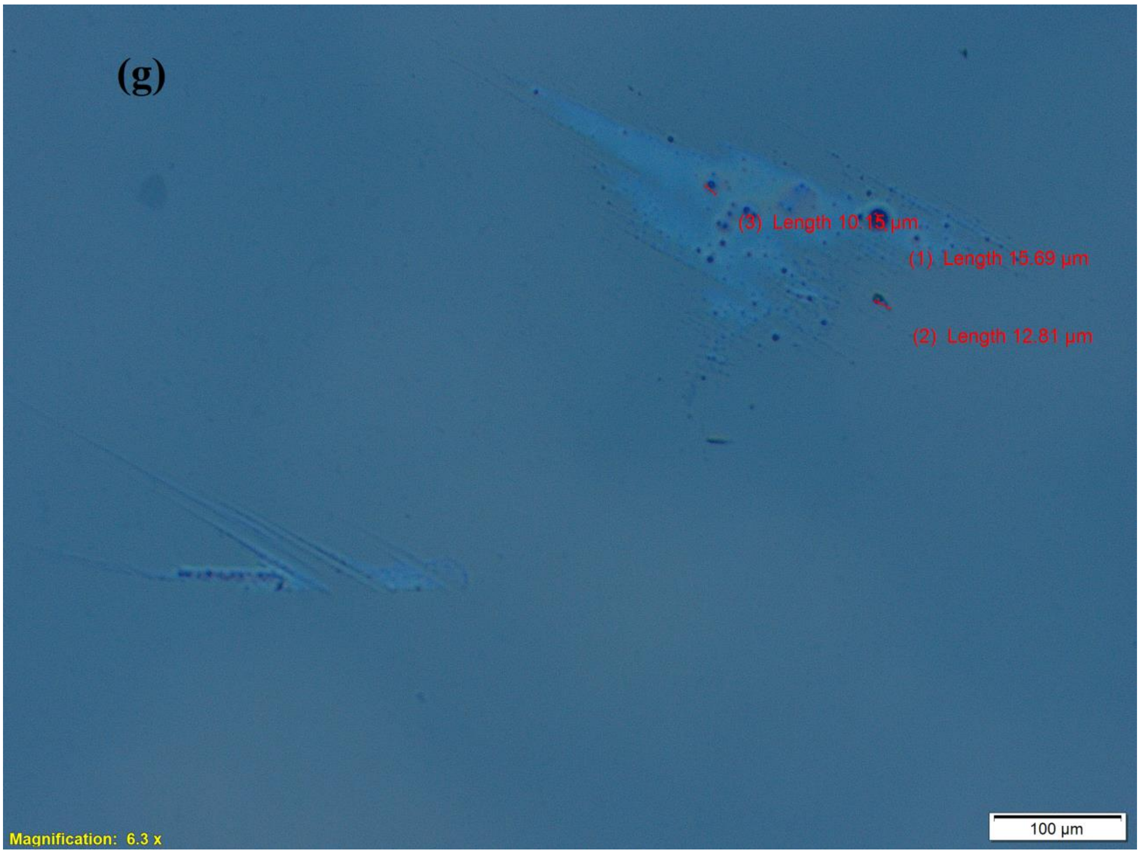
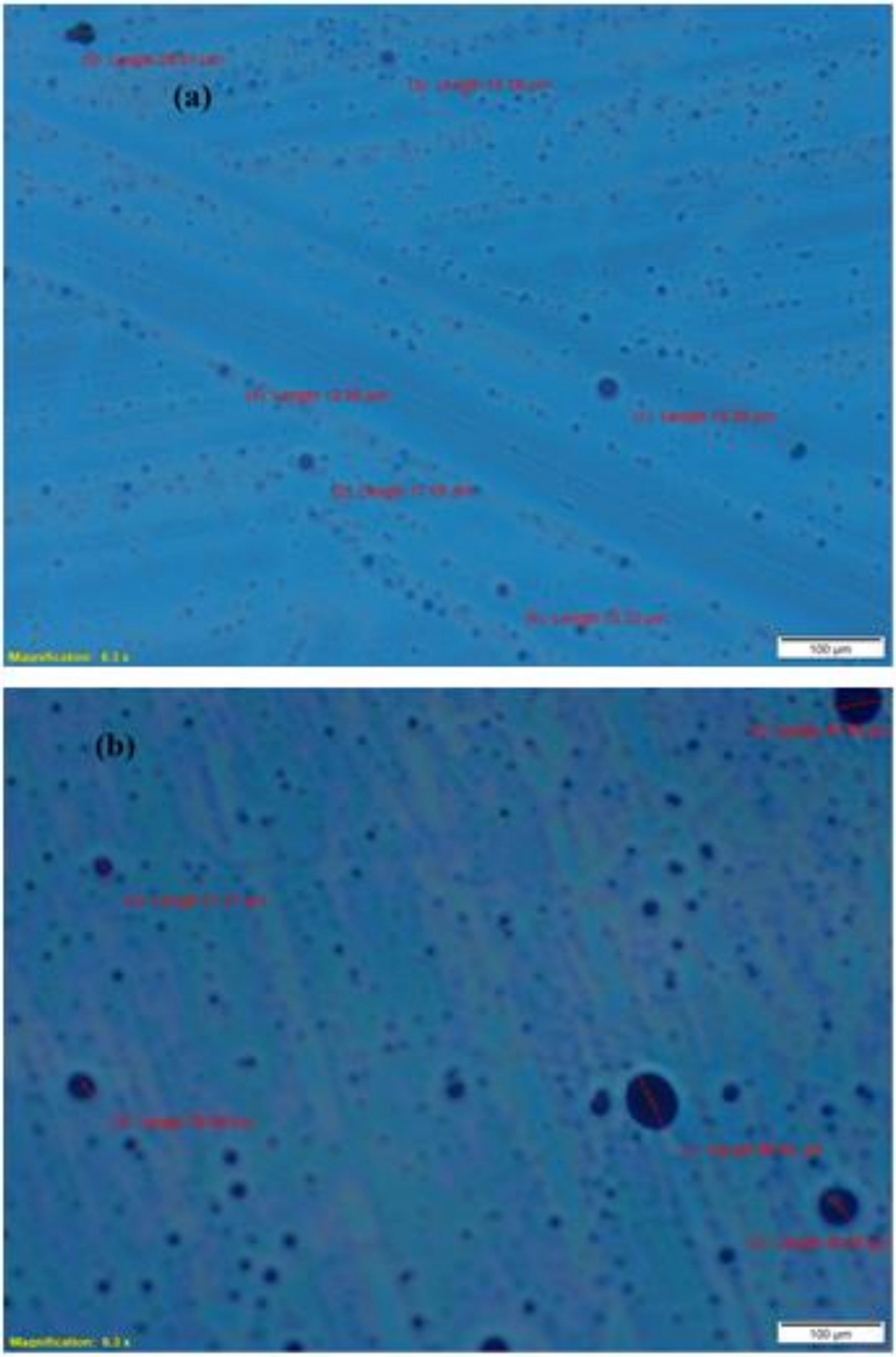
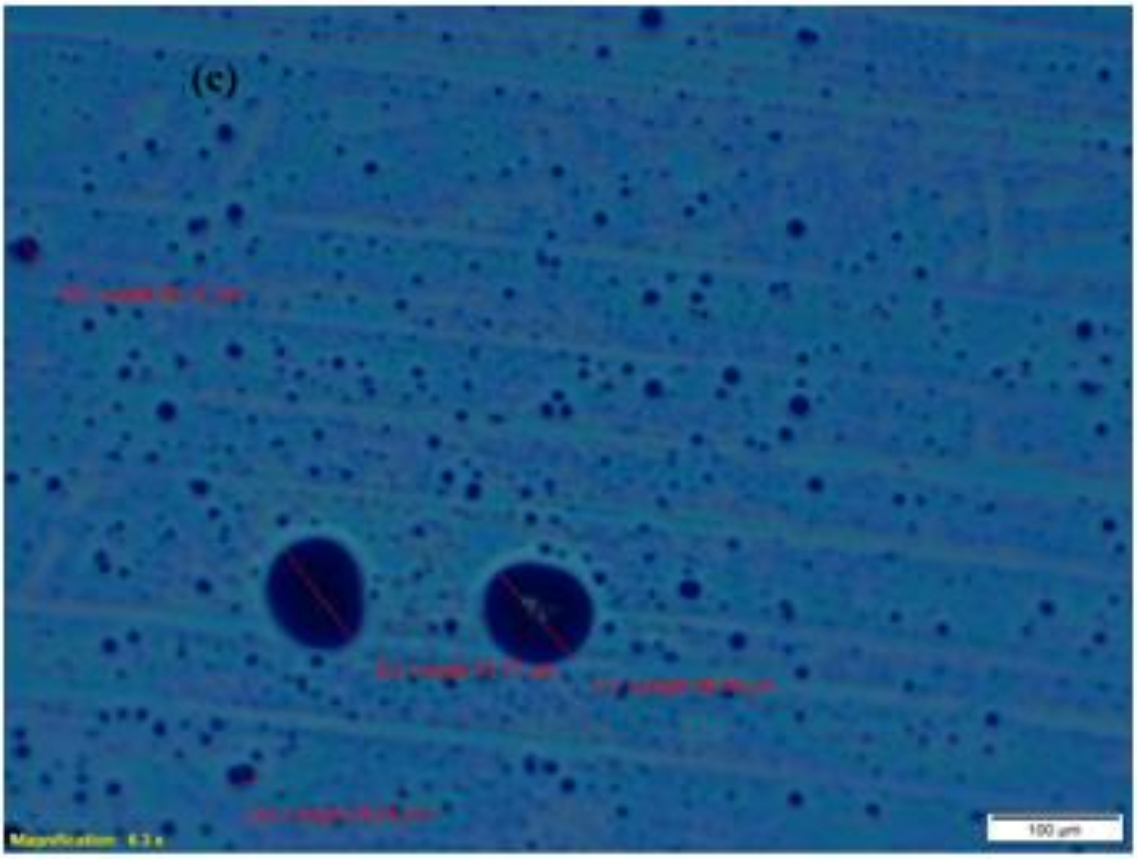
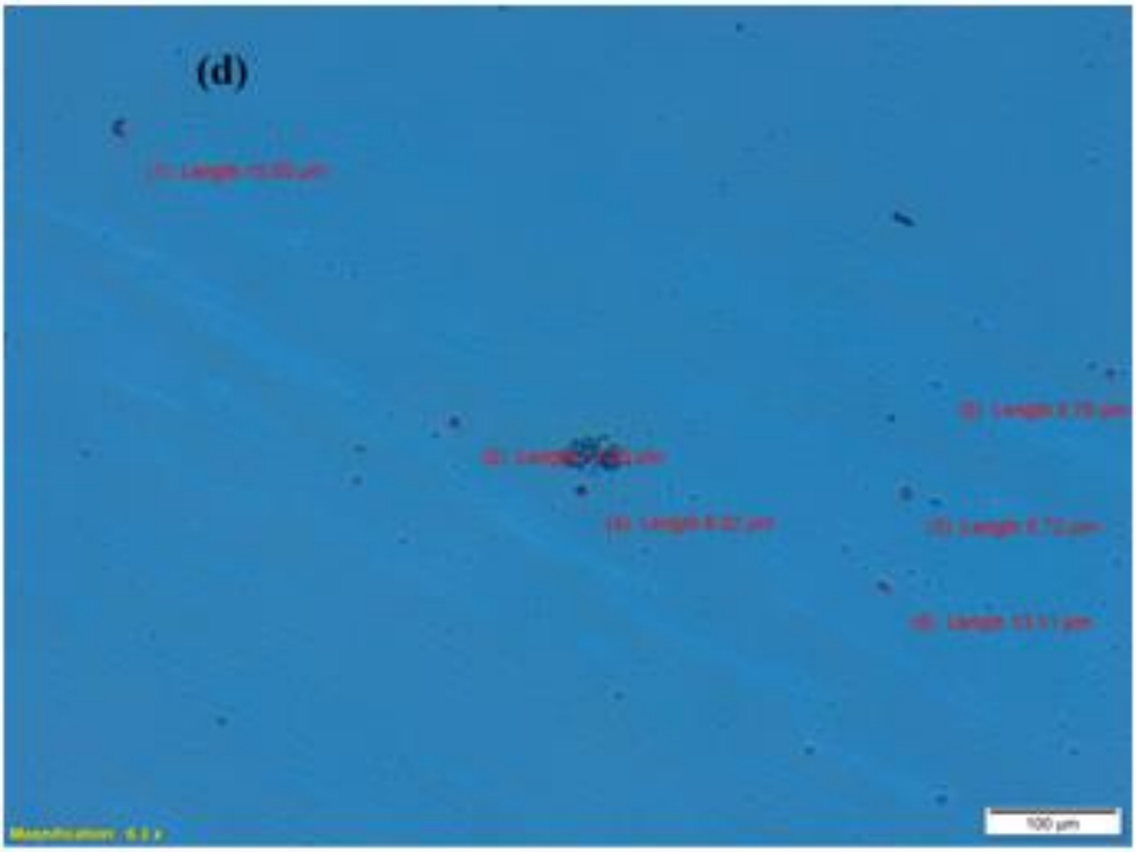


Figure 25: Precipitated asphaltenes in different samples at 50°C. (a) crude oil + n-C_7; (b) crude oil + S.A. 2.5% + n-C_7; (c) crude oil + S.A. 5.0% + n-C_7; (d) crude oil + S.A. 10% + n-C_7; (e) crude oil + I.A. 2.5% + n-C_7; (f) crude oil + I.A. 5.0% + n-C_7; (g) crude oil + I.A. 10% + n-C_7.

The crude oil samples at 50°C were left 24h in water-bath and then observed in the microscope in order to verify if the particles growth have increased or decreased when the samples were kept in high temperature (see figure 26) as well as to compare their size with crude oil samples kept 12h in the water bath and crude oil samples kept at room temperature.


(a)
Magnification: 6.3 x
100 µm
(b)
Magnification: 6.3 x
100 µm


(c)
Magnification: 6.3 x
100 µm


(d)
Magnification: 6.3 x
100 µm

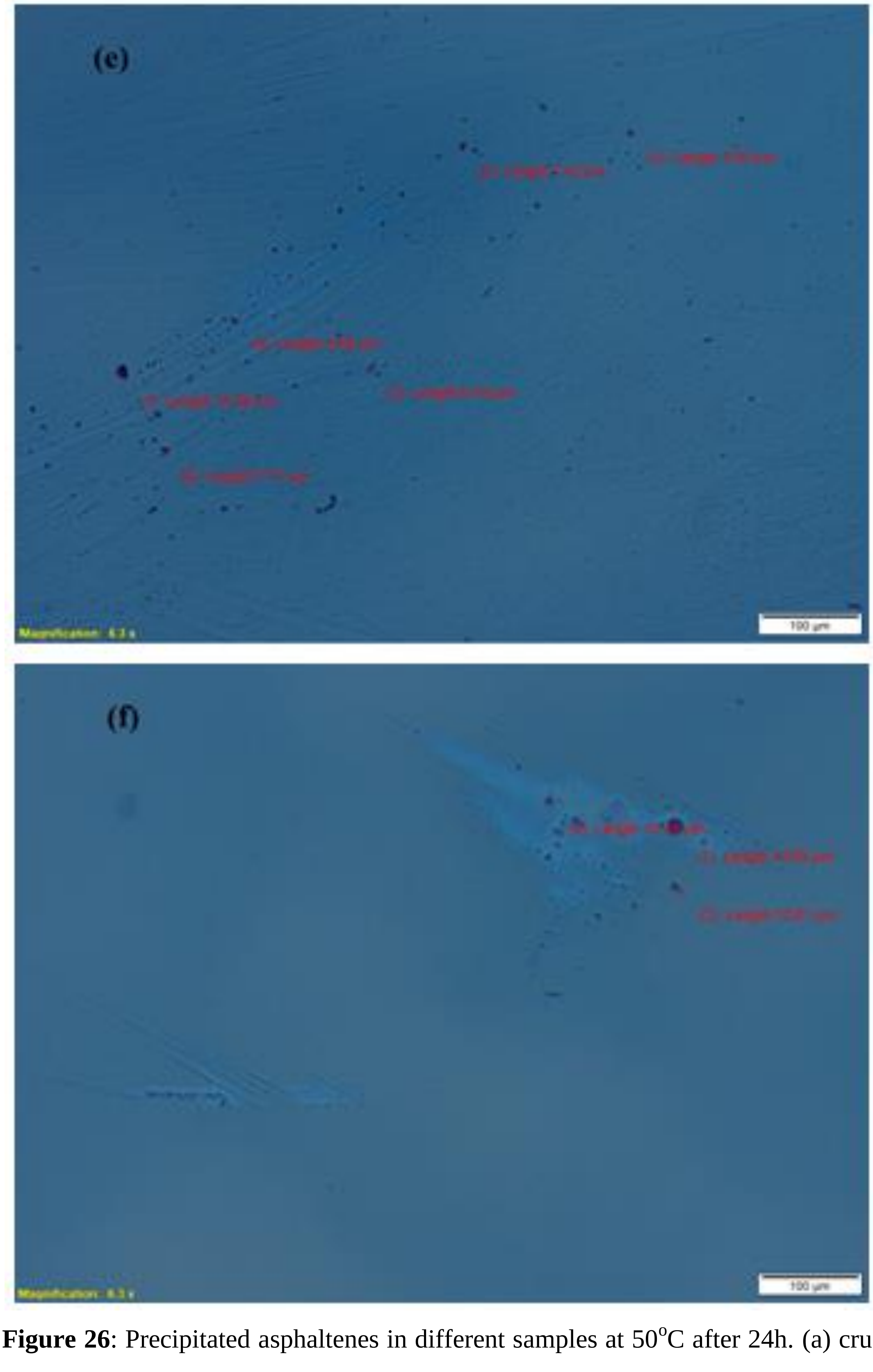


Figure 26: Precipitated asphaltenes in different samples at 50^{o}C after 24h. (a) crude oil + n-C_7; (b) crude oil+ S.A. 2.5% + n-C_7; (c) crude oil + S.A. 5.0% + n-C_7; (d) crude oil + S.A. 10% + n-C_7; (e) crude oil + I.A. 2.5% + n-C_7; (f) crude oil + I.A. 5.0% + n-C_7; (g) crude oil + I.A. 10% + n-C_7.

3.6. Reduction of asphaltene precipitation

In this research, the precipitation reduction percentage was determined based on mass of asphaltene. These masses were extracted from the crude oils samples (without and with inhibitors) through *IP 143* modified procedure because it is a method that involves variation of temperature. In this case, all samples were heated under reflux at 50ºC. After extraction of asphaltene in all samples, their masses were weighed. Then, they were dried for 24h in an oven at same temperature and afterwards all oil samples were left resting in room temperature again for 24h. The samples were kept in an evaporating vessel to avoid air contamination which can affect the final weight of asphaltene. These steps were repeated three times in order to obtain the standard deviation through equation 2 as shown in the results on table 10.

Then, the precipitation reduction versus solvent inhibitor concentration cross-plots was calculated based on the equation 4:

Equation 4

$$\text{Precipitation reduction (\%)} = \frac{\text{asphaltene blank} - \text{asphaltene treated}}{\text{asphaltene blank}} * 100$$

Asphaltene blank and treated were considered the mass (g) of dried asphaltene obtained from blank oil (without inhibitor) and treated oil (with different inhibitors concentrations) respectively. The total mass for blank and treated asphaltene was calculated through the difference of the asphaltene masses weighed before drying and after drying and cooling down, the extracted asphaltene.

CHAPTER IV: Results and discussions

4.1. Quantification of asphaltene precipitation

Table 7: SD of masses of dried asphaltene obtained through equation (1).

$M1_{(g)}$	$M2_{(g)}$	$M3_{(g)}$	$M_{average(g)}$	SD
0.14	0.15	0.13	0.14	0.01

Table 7 shows the SD of mass of dried asphaltene. According to the results, it is possible to deduce that every single number in the data set for the crude oil sample in study is almost the same with the consecutives measurements ($M1 \approx M2 \approx M3$). Therefore, it means that the values found in the statistical data set (M1, M2, M3) are close to the mean of the data set, on average, what eventually shows that the measurements were accurate. Equation 2 was used to obtain the result of 6.09 for asphaltene content. Based on the result, it is reasonable to infer that the crude oil in study has unstable asphaltene, as discussed above, high asphaltene content may describe stable asphaltenes and low asphaltene content may describe unstable asphaltene into the crude oil. Nonetheless, asphaltene content result may prone to false future asphatenic problems, since the test used to obtain asphaltene content is not very sensitive due to interference of dirt and solids contaminants in the crude oil, therefore making the results sometimes inaccurate.

4.2. Evaluation of asphaltene stability in the crude oil samples

Table 8: Results of SARA analysis.

SARA analysis result (%weight)	
Saturates	63.056
Aromatics	17.448
Resins	13.409
Asphaltenes	6.087

Table 9: Hydrocarbon constituent ratio and CII results.

Sample	***Asphaltene/Resin***	***Saturate/Aromatic***	***CII***
Crude oil	0.467	3.614	2.241

According to the above results, it is possible to notice that the crude oil sample has predominance in saturates compounds rather than aromatics. It means asphaltene has weak solvency resulting in more unstable asphaltene into the oil. On balance, the sample has a low asphaltene/resin ratio (resins compounds are greater than asphaltene) resulting in a good colloidal stabilization. From CII of 2.241 obtained through equation (3), the crude oil has demonstrated unstable oil system which means that the South African oilfield can face huge asphaltene problems in the future.

Correlation between CII and SARA components.

As above mentioned, asphaltene is the heaviest and most polar constituent in the crude oil. Through the results (table 8 and 9), it can be deduced that asphaltene component is inversely proportional to CII, since the result has shown low asphaltene content but the CII was high, which shows an agreement with the results available in the literature. Several researches have reported that oils with low asphaltene content are most likely to precipitate rather than those with high asphaltene content.

Resin is a dark brown colored fraction, polar with heteroatoms as N, O, S (similar to the asphaltenes however with lower molecular weight). As discussed above, its presence is very important to stabilize asphaltene as well as prevent asphaltene aggregation; therefore, it is assumed that an increment in resin content will decrease the CII (Ashoori *et al*., 2016). From table 8 and 9, the results demonstrated a low resin value which cannot reduce the CII, resulting in high instability.

Aromatic class is a viscous dark fairly red liquid formed from hydrocarbon, mono-, di-, poli-aromatics, and alky-substitution as well as heteroatoms (S, O, N) (Keshmirizadeh *et al*., 2013). Due to their polarity, aromatics also play an important role in asphaltene stability. Furthermore, they act as bridge between the micelle mixtures and saturates, improving the mixed micelle dispersion in saturate fraction (Ashoori *et al*., 2016). According to the above results, the oil in study has low aromatic value which can also lead to high CII.

Saturates is the non-polar fraction in the crude oil, made from paraffin's and diamonds oils. It is a whitish translucent solution that can be either easily distinguished or separated from the rest fractions of crude oil owing to any presence of π-bonds into saturates molecules (Keshmirizadeh *et al*., 2013). High saturate content in the crude oil lead to low aromatic and resin content, resulting in high CII (Ashoori *et al*., 2016), which is in agreement with the saturate value obtained.

All in all, based on the above results it can be assumed that the four fractions affect the CII and consequently the crude oil stability. High content of polar fractions (asphaltene, resins and aromatics) affect positively the oil stability while high non-polar fraction (saturate) leads to saturation of crude oil, resulting in instable oil system.

4.3. Detection of asphaltene precipitation onset

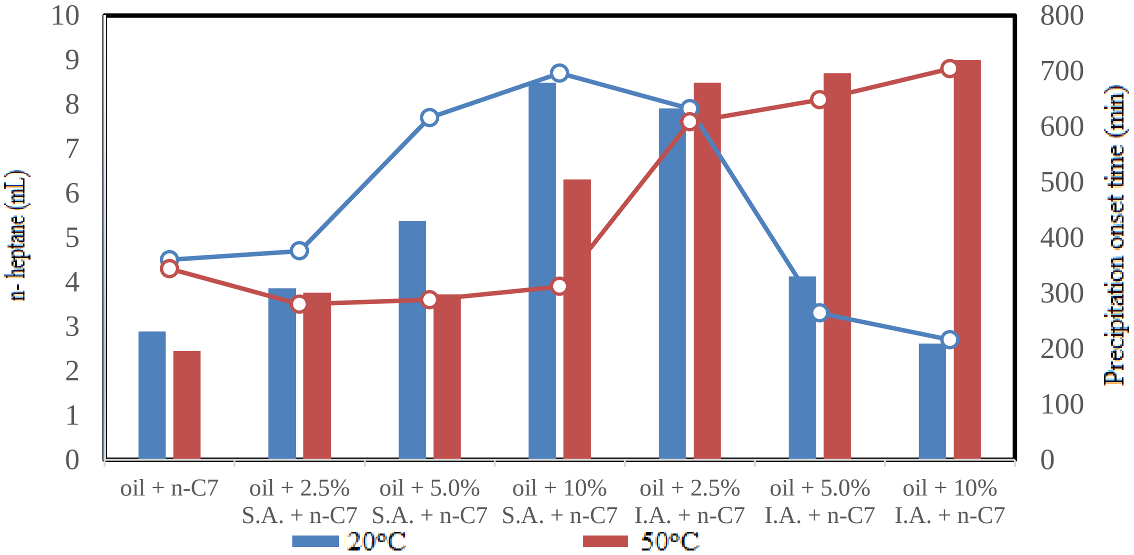


Figure 27: Volume of n-C_7 used to achieve precipitation onset time in different oil samples.

Asphaltene precipitation onset is defined as the time needed to appear the first 0.5µm asphaltene particle in the crude oil (Maqbool *et al*., 2010), in other words, it is the point where asphaltene becomes unstable (Kashefi *et al*., 2016).

In this study, evaluation of asphaltene precipitation was divided into four (4) steps as shown microscope images from figures 10 to 16 (at 20°C) and 17 to 23 (at 50°C): (*i*) assessment of crude oil samples before any disturbance occurs; (*ii*) particles nucleation, where asphaltene clusters start to be formed due to precipitant addition; (*iii*) growth of asphaltene clusters; (*iv*) generation of larger aggregates that flocculate and form visible particles on microscope (assumed as asphaltene precipitation onset time).

The main mechanism for asphaltene precipitation phenomenon depicts destabilization of asphaltene nano-aggregates particles from the crude oil through addition of a precipitant (Maqbool *et al.,* 2010). In this work, 99% vol. n-heptane was continuously added in crude oil samples without and with solvent inhibitors at different temperatures (20 and 50ºC) until formation of larger particles detectable on microscope. From the figure 27 (columns), it is clear that the precipitation onset time in the samples with inhibitors is by far greater than samples without them; however, it is also notable that both solvents inhibitors in different concentrations as well as temperature affect differently the delay time to precipitate asphaltene. At 20ºC (blue column), the microscope results show that the onset time for blank sample (without inhibitor) is 231min when 4.5mL of n-heptane is added (blue line). When inhibitor is added into the fluid, the highest precipitation onset point peak can be observed into the sample with oil + 10% S.A. + n-C_7 when 8.4mL of precipitant is added (blue line) after 679min (blue column). On the other hand, the lowest onset point was verified into the sample with oil + 10% I.A. + n-C_7 when 2.7mL of precipitant was added (blue line) at 209min (blue column). Moreover, the graphs show that as long as S.A. concentration increase, the delay time for asphaltene precipitation also improve while I.A shows an opposite behavior, as long as its concentration increase, the delay time for asphaltene precipitation reduce. The amount of n-heptane added continuously (until formation of big particles- >0.5µm) into the samples containing chemical inhibitors have determined the capability of the S.A. and I.A with different concentrations to delay asphaltene precipitation onset time in the following order: (1) 10% S.A, (2) 2.5% I.A, (3) 5% S.A, (4) 5% I.A, (5) 2.5% S.A and 2.5% I.A respectively.

Several researches have already reported that each polar head group of a solvent inhibitor shows different potential to connect itself to asphaltene molecules, since the polarity of these groups describe the power of the bond between asphaltene particles and the inhibitor (Karambeigi. *et al*., 2016; Kashefi *et al*., 2016).

S.A present high performance when compared with I.A due to the extra hydroxyl functional group (-OH) joined to benzoic ring. It is assumed that the reaction as well as the join of the inhibitor polar functional group to the asphaltene particles leads to an inhibitor- asphaltene stable system (Karambeigi *et al*., 2016). Therefore, any increment in S.A concentration will improve stability of asphaltene particles. On balance, I.A does not have –OH but has carboxyl groups (-COOH). It is known that –OH has greater potential to stabilize asphaltene rather than –COOH (Kashefi *et al*., 2016). I.A at lower concentration (2.5% I.A) occupied the second position regarded to stabilize asphaltene particles but any increment in its concentration accelerated the asphaltene precipitation. Under existence of hydrogenous bonding, when there is an increment in the inhibitor concentration, the tendency of self-association also increases (Karambeigi *et al*., 2016), therefore, when I.A concentration is increased into the liquid oil the potential to self-association between solvent-solvent has stronger interaction compared to inhibitor-asphaltene.

At 50ºC (red column), the results show that the onset time of samples with S.A reduced significantly. According to previous studies, the precipitation onset time at high temperature is shorter because the viscosity of oil-precipitant mixture reduces due to heat conditions, consequently the diffusivity power of the particles into the oil increase and causes faster aggregation of asphaltene clusters (hence, reducing the asphaltene onset time) (Maqbool *et al*., 2010).

However, samples with I.A inhibitor have shown another behavior, it means, for all concentration the results demonstrated an increment on the delay time for asphaltene precipitation. In addition, as long as I.A concentration was increased, the precipitation onset point improved dramatically. This phenomenon can be explained due the fact that S.A is instable in excessive heat conditions while I.A is thermally stable.

4.4. Solvents/ precipitant mixtures assessment

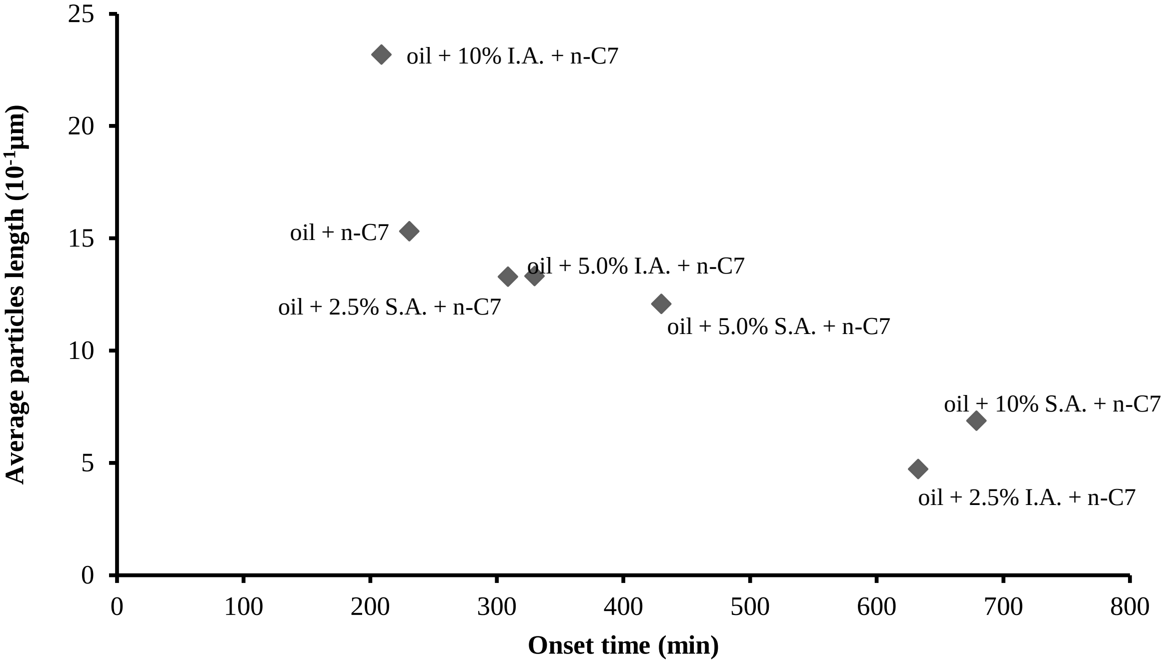


Figure 28: Average of asphaltene particles length as a function of asphaltene precipitation onset time at 20ºC.

.

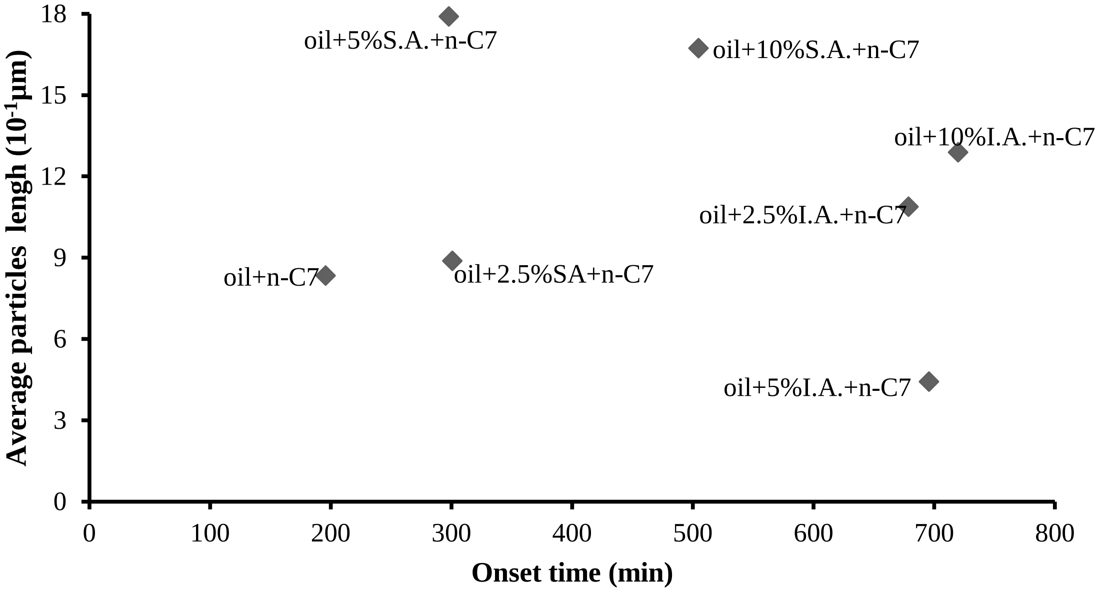


Figure 29: Average of asphaltene particles length as a function of asphaltene precipitation onset time at 50ºC.

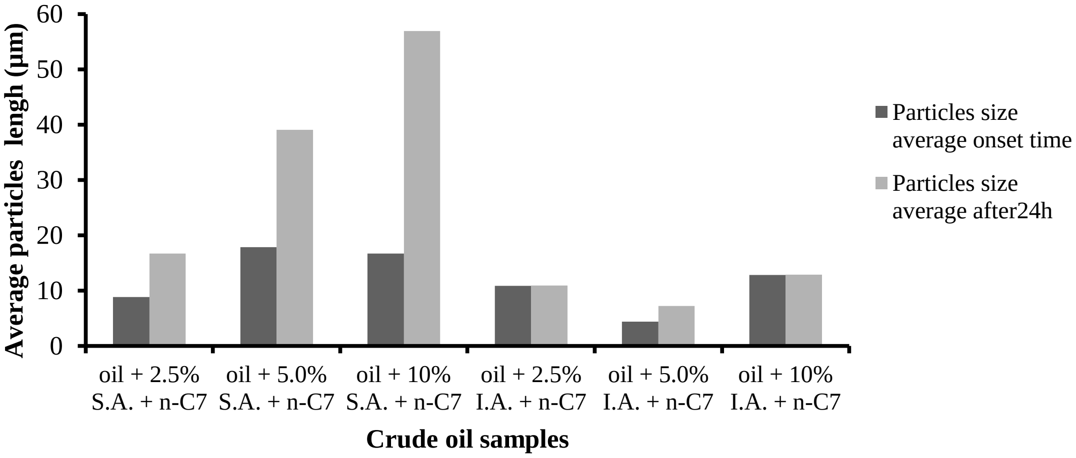


Figure 30: Comparison between the asphaltene particles sizes on onset point and after 24h (at 50ºC).

In this work, to assess solvent-precipitant mixture efficiency, the wide particles size distribution as well as the continuous growth of asphaltene aggregates at different temperature when different concentrations of chemicals were added was evaluated. It clearly shows that distinct types of aggregates structure can be found into the fluid (see figures 24, 25 and 26), which is assumed as the main key either to characterise the inhibitors effects in the aggregation kinetics or control the asphaltene stability into the crude oil samples.

The average sizes of asphaltene clusters (measurement of the length in µm) as function of onset time as well as variation of temperature is shown in figure 28 and 29 for two (2), S.A. and I.A. in different concentrations (2.5, 5.0 and 10%). The microscope has detected particles with nearly 0.5µm or larger. At 20ºC (figure 28) the size distribution of asphaltene cluster covers a range from ~0.5 to ~2.3µm. The biggest size is verified in crude oil sample with 10% I.A. (~2.318µm) after 209min of continuous addition of n-heptane (2.7mL). In addition to that, the smallest size is observed in oil sample with 2.5% I.A. (~0.472µm) after 633min of continuous addition of 7.9mL of n-C_7. Furthermore, the results in figure 28 demonstrate that an increment in SA concentration, decrease the aggregates size and slow down the aggregation phenomenon while an increment in I.A. concentration leads to an appositive scenario (see figure 24). Thus, the deduction of inhibitor capability made in the previous section is reasonable and apply at room temperature.

At 50ºC (figure 29) the size distribution of asphaltene clusters start from ~0.5 up to ~1.8µm. The biggest size is verified in crude oil sample with 5% S.A. (~1.789µm) after 298min of continuous addition of n-heptane (3.6mL). Moreover, the smallest size is observed in oil sample with 5% I.A (~0.442µm) after 696min of continuous addition of 8.1mL of n-C_7 (see figure 25). In addition, the results in figure 29 shows that there is no a linear behavior upon the growth of aggregates size and distribution of asphaltene aggregates when chemical inhibitors concentrations are changed. Hence, all samples were heated for 24h (same temperature) and then the particles aggregates sizes were observed and compared with the sizes of the ones obtained in the onset point (figure 30). A huge increase in the asphaltene particles contained in the S.A. solvents was observed, mostly when the inhibitors concentrations were increased due to stronger asphaltene molecules interaction. Nonetheless, the precipitated amount of asphaltene remained the same. For oil samples containing I.A. solvent a small increment in the asphaltene particles diameter was observed (see figure 26), which proves that I.A is really stable in high temperature while S.A is not.

4.5. Reduction of asphaltene precipitation

Table 10: SD results of the weights of asphaltene in different samples.

Samples	**M1$_{(g)}$**	**M2$_{(g)}$**	**M3$_{(g)}$**	**M $_{(g)\text{average}}$**	**SD**
oil + n-C_7	0.60	0.61	0.63	0.61	0.01
oil + 2.5% S.A. + n-C_7	0.20	0.22	0.21	0.21	0.01
oil + 5.0% S.A. + n-C_7	0.30	0.36	0.32	0.33	0.02
oil + 10% S.A. + n-C_7	0.45	0.48	0.48	0.47	0.01
oil + 2.5% I.A. + n-C_7	0.25	0.23	0.26	0.25	0.01
oil + 5.0% I.A. + n-C_7	0.11	0.11	0.14	0.12	0.01
oil + 10% I.A. + n-C_7	0.16	0.14	0.16	0.15	0.01

Table 10 shows the SD calculated for the asphaltenes weights coming from the seven samples in study. SD provides an indication of how far a single value(s) vary or deviate from the mean. According to the SD results, it's possible to see that the The SD of the 6 measurements (the first is the control) made are quite small showing that the values obtained are around the average for each measurement in triplicate. This means in other words that the averages of the measurements in triplicate, both with increasing percentages of SA and IA, are different between themselves and the control. Furthermore, the table shows that the asphaltene mass obtained in the sample oil + n-C_7 is greater than the six samples with different solvents concentrations.

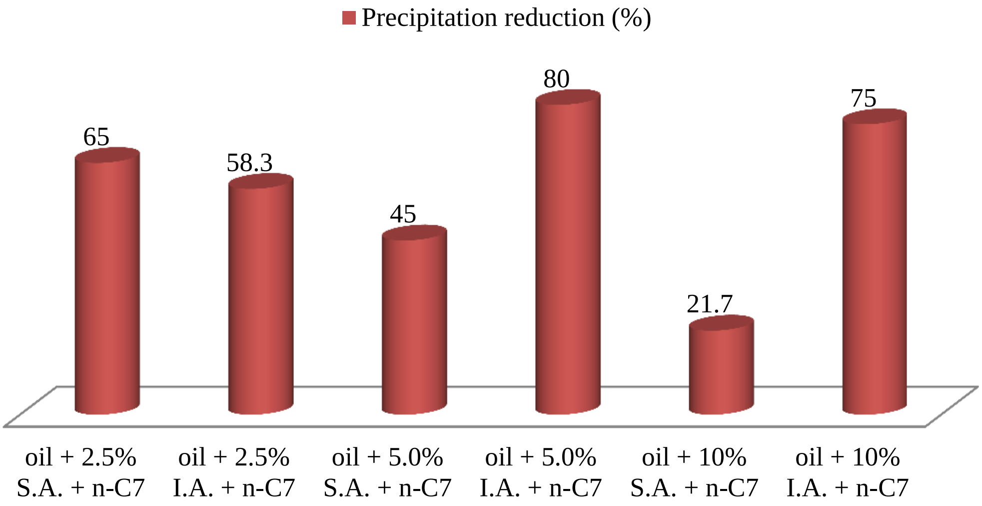


Figure 31: Assessment of solvent inhibitors effects in crude oil samples.

Effects of chemical inhibitors in the reduction of asphaltene precipitation when variation in temperature occurs are shown in the figure 31. The results demonstrated that I.A inhibitor has better performance rather than S.A inhibitor; nevertheless 2.5% S.A has shown high percentage when compared to 2.5% I.A. The strongest effectiveness in inhibition of asphaltene precipitation was observed at 5% I.A. (80%), while the weakest efficiency was verified at 10% S.A. (21.7%). According to the literature S.A due to its chemical structure (presence of –OH and –COOH groups connected to the benzoic ring) provides better capability to stabilize asphaltene particles into the crude oil. The –OH functional groups generate a stronger planar phenol structure which improves the π–π interaction stability between inhibitor and asphaltene molecules, what was observed with S.A at room temperature (Karambeigi *et al.*, 2016).

However, results have demonstrated that S.A is sensitive to high temperatures (mainly in high concentrations), thereby decreasing its capability to inhibit asphaltene precipitation. Although I.A less capability to stabilize asphaltene particles when compared to S.A, it also has a chemical structure (presence of two –COOH groups connected to the benzoic ring) which stabilize asphaltene precipitation (Karambeigi *et al.*, 2016). Results proved that I.A. inhibition capability can be either improved or remained unaltered when variation in temperature occur since I.A demonstrated to be thermally stable in excessive heat.

CHAPTER V: Conclusions and recommendations

5.1. Study summary

In the present research, a deep study was developed in crude oil samples from one of the South African oil fields in order to evaluate the probability of asphaltene precipitation to occur in this field and then assess promising chemical solvents that can be used to inhibit this phenomenon when changes in temperature and fluid composition happen. Hence, the study was divided into the three (3) following parts:

(i) Investigation of the asphaltene content into the crude oil samples;
(ii) Characterization of the crude oil samples and determination of the stability of the asphaltene-oil system;
(iii) Assessment of the chemical inhibitors efficiency in oil samples in different concentrations as well as temperature.

5.2. Conclusion

The main focus of this study was to evaluate and test the capability chemical with different concentration to inhibit asphaltene precipitation in South African oilfields when changes in the thermodynamic parameters occur. Phenomenon which can be observed at all stages of oil production from the well to the refining. Nevertheless, this research just covers asphaltene precipitation conditions during the transportation.

Therefore, two solvents (salicylic acid and *iso*-phthalic acid) were selected and tested in crude oil samples to determine its potential to reduce asphaltene precipitation. Results proved that 5% I.A. has the highest potential with 80% to reduce asphaltene precipitation among the other concentrations and inhibitor.

It also confirmed that temperature has a great impact in one hand, in the fluid composition since variation in temperature can change the fluid viscosity, which then affects the speed of asphaltene aggregation which can either increase or reduce the asphaltene precipitation onset time. However, on the other hand, temperature has a great role on the performance of chemical solvents to inhibit asphaltene precipitation. For example, in low temperature S.A demonstrated better performance than I.A while in high temperature, I.A. shows the best performance.

Furthermore, for the experimental conditions described in this work, both inhibitors proved to provide high potential to inhibit asphaltene precipitation when added before asphaltene aggregation starts, although in different concentration and temperatures. This potential is explained due to the presence of –OH and –COOH (for S.A.) and –COOH (for I.A.) as discussed in the previous section.

Results of precipitation reduction calculation demonstrated that the inhibitor potential order to prevent asphaltene precipitation in the crude oil sample was the following: (1) 5% I.A., (2) 10%I.A., (3) 2.5% S.A., (4)2.5% I.A., (5) 5% S.A. and (6) 10% S.A. However, it is important to have in mind that its performance can vary from crude to crude and according to thermodynamic parameter conditions.

5.3. Recommendations and Future works

Based on the results obtained in this study, the present research recommends the following point for future works:

- To assess and test the same chemical solvents proposed in this study in others crude oil samples with different sources as well as different API° class of crude oil;
- To develop a similar study with crude oil samples coming from the same South African oilfields extending the temperature (since in this study solvents effects was observed only at 20 and 50ºC) and if necessary, changing the inhibitor concentrations;
- To investigate the potential of asphaltene inhibition of S.A. and I.A. at reservoir conditions since as discussed in the literature, asphaltene problematic is more predominant inside the rock formation and down hole.
- A study should be based in developing more structure with more -OH and less –COOH groups in order to investigate the inhibitor behavior when variations in these groups occurs.

REFERENCES

- Abedini, A., Ashoori, S., Torabi, F., Saki, Y. & Dinarvand, N. (2011). **Mechanism of the Reversibility of Asphaltene Precipitation in Crude Oil.** Journal of Petroleum Science & Engineering. Vol. 78. 316-320pp.
- Almehaideb, R. (2004). **Asphaltene Precipitation and Deposition in Near Wellbore Region: A Modelling Approach**. Journal of Petroleum Science & Engineering. Vol. 42. 157-170pp.
- Artola, P., Perreira, F., Adjiman, C., Galindo, A., Muller, R., Jackson, G. & Haslam, A. (2011). **Understanding the Fluid Phase Behaviour of Crude Oil: Asphaltene Precipitation**. Fluid Phase Equilibria. Vol. 306. 129-136pp.
- Ashoori, S., Sharifi, M., Masoumi, M. & Salehi, M. (2016). **The Relationship Between SARA Fractions and Crude Oil Stability**. Egyptian Journal of Petroleum. Vol. 26. 209-213pp.
- Asomaning, S. (2003). Test Methods for Determining Asphaltene Stability in Crude Oils. Petroleum Science and Technology. Vol. 21(3). 581-590pp.
- ASTM, D., 2007. **Standard test method for characteristic groups in rubber extender and processing oils and other petroleum-derived oils by the clay-gel absorption chromatographic method**. Annual Book of ASTM Standards, Philadelphia, Sec, 5.
- Chrisman, E., Lima, V. & Menechini, P. (2012). **Asphaltenes – Problems and Solutions in E&P of Brazilian Crude Oils**. Federal University of Rio de Janeiro/DOPOLAB. Brazil. 1-22pp.
- Colaiocco S. and Farrera M., 2001. **Determination of Asphaltene Content in Crude Oil by Attenuated Total Reflectance Infrared Spectroscopy**. *Fifteenth International Forum Process Analytical Chemistry (IFPAC)*. Amelia Island, Florida, U. S. A.
- Dehaghani, A. & Badizad, M. (2017). **Inhibiting Asphaltene Precipitation from Iranian Crude Oil Using Various Dispersants: Experimental Investigation Through Viscometer and Thermodynamic Modelling**. Fluid Phase Equilibria. Vol. 442. 104-118pp.
- Eigner, M. (2016). Asphaltenes. [Online] Available from: http://www.oilfieldwiki.com/wiki/Asphaltenes [Accessed on 29th March 2017]

- Elochukwu, O., Saaid, I. & Pilus, R. (2014). **Organic Deposit Remediation Using Environmentally Benign Solvents: A Review**. ARPN Journal of Engineering and Applied Sciences. Vol. 9(10). 1930-1936pp.
- Elochukwu, O. & Mahmud, H. (2015). **An Environmentally Friendly Solvent Mix for Asphaltene Deposit Removal**. ARPN Journal of Engineering and Applied Sciences. Vol. 10(22). 10555-10565pp.
- Hasssanvand, M., Shahsavani, B. & Anooshe, A. (2012). **Study of Temperature Effect on Asphaltene Precipitation by Visual and Quantitative Methods**. Journal of Petroleum Technology and Alternative Fuels. Vol. 3(2). 8-18pp.
- IP 143/01 ASTM D650-00 Standard Procedure. (2001). **Determination of Asphaltene in Crude Petroleum and Petroleum Products**. 1-7pp.
- Junior, R., Ferreira, M. & Ramos, A. (2006). **Inhibition of Asphaltene in Brazilian Crude Oils Using New Soluble Amphiphiles**. Journal of Petroleum Science and Engineering. Vol. 51. 26-36pp.
- Kashefi, S., Shahrabadi, A., Jahangiri, S., Lotfollahi, M. & Bagherzadeh, M. (2016). **Investigation of The Performance of Several Chemical Additives on Inhibition of Asphaltene Precipitation**. Energy sources, part a: recovery, utilization, and environmental effects. Vol. 38(24). 3647-3652pp.
- Keismirizadeh, E., Nikazar, M. & Kharrat, R. (2013). **Determination of Saturates, Aromatics, Resins and Asphaltenes (SARA) Fractions in Iran Crude oil Sample with Chromatography Methods: Study of the Geochemical Parameter**. Journal of Applied Chemical Research. Vol. 7(4). 14-24pp.
- Kokal, S. et al. (2005). **Asphaltene Precipitation in High Gas-Oil Ratio Wells**. Saudi Aramco Journal of Technology.
- Leontaritis, K. & Mansoori, G. (1987a). **Asphaltene Flocculation During Oil Production And Processing: A Thermodynamic Colloidal Model**. Society of Petroleum Engineers of AIME. 149-158pp.
- Mahmoudi, B. & Zare-Reisabadi, M. (2015). **Experimental Study Of Temperature Effect On Onset Pressure Of Asphaltene In Live Oil**. Petroleum & Coal. Vol. 57(4). 346-352pp.

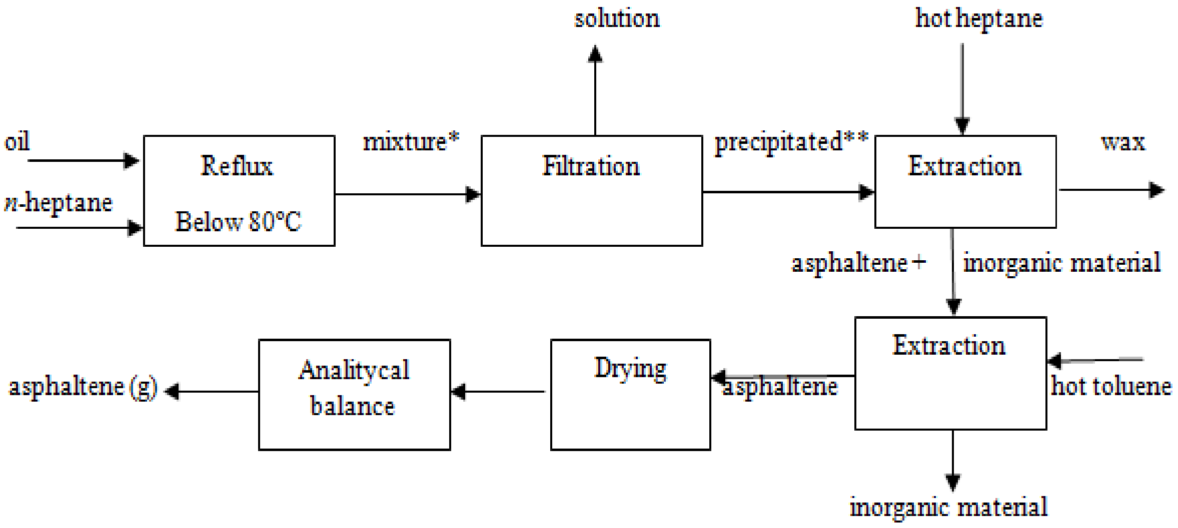
- Maqbool, T., Srikiratiwong, P. & Fogler, H. (2010). **Effect of Temperature on the Precipitation Kinetics of Asphaltenes**. Energy & Fuels Article. Vol. 25. 694-700pp.
- Meraikhi, A. (2015). **An Experimental and Theoretical Investigation of Asphaltene Precipitation and Aggregation Kinetics in Model Oil Systems**. The Petroleum Institute.
- Mirzayi, B., Mousavi-Dehghani, S. & Sobhi, G. (2012). **Prediction of Solvent Effect on Asphaltene Precipitation at Reservoir Conditions**. Journal of Petroleum Science and Technology. Vol. 2(2). 17-24pp.
- EASTMAN. (2015). *Material Safety Data Sheet: Iso-phthalic Acid powder*. No. EAN 903233. P1837001. Eastman Chemical Company. Kingsport
- ScienceLab. (2005). *Material Safety Data Sheet: Salicylic Acid powder*. No. 69-72-7. ScienceLab.com, Inc. Houston, Texas
- Mullins, O. (2016). **Asphaltene**. The Defining Series. Oilfield Review. Schlumberger.
- Palermo, L. (2013). **Development of Multifunctional Formulations for Inhibition of Waxes and Asphaltene Deposition**. Brazilian Journal of Petroleum and Gas. Vol. 7(4). 181-192pp.
- Panuganti, S. (2013). **Asphaltene Behavior in Crude Oil Systems**. Rice University. Houston, Texas.
- Paraskova, T. (2017). South Africa: The Next Hot Spot for Offshore Oil Exploration. [Online] Available from https://oilprice.com/Energy/Crude-Oil/South-Africa-The-Next-Hot-Spot-For-Offshore-Oil-Exploration.html [Accessed on 2nd December 2017]
- Petroleum Agency SA. (2013). **Onshore Karoo Basins**. [Online] Available from: http://www.petroleumagencysa.com/index.php/25-frontiergeology/53-onshore [Accessed on 2nd December 2017]
- Rastgoo, A. & Kharrat, R. (2017). **Investigation of Asphaltene Deposition and Precipitation in Production Tubing**. International Journal of Clean Coal and Energy. Vol. 6. 14-29pp.
- SAMSA. (2011). **Offshore Oil and Gas- Industry Profile**. Centre for Policy and Regulation. South Africa. 1-13pp.

- Shirani, B., Nikazar, M., Naseri, A. & Mousavi-Dehghani, S. (2012a). **Modeling of Asphaltene Precipitation Utilizing Association Equation of State**. Fuel. Vol. 93. 59-66pp. doi:10.1016/j.fuel.2011.07.007.
- Shirani, B., Nikazar, M., Naseri, A. & Mousavi-Dehghani, S. (2012b). **Prediction of Asphaltene Phase Behavior in Live Oil with CPA Equation of State**. Fuel. Vol. 97. 89-96pp. doi:10.1016/j.fuel.2012.02.016.
- SOAGA. (2014). **Oil and Gas Statistics**. [Online] Available from: https://www.saoga.org.za/oil-gas-hubs/upstream-oil-gas-south-africa [Accessed on 2nd December 2017**]**
- Solaimany-Nazar, A. & Zounnouri, A. (2011). Modeling of asphaltene deposition in oil reservoirs during primary oil recovery. Journal of Petroleum Science and Engineering. Vol. 75. 251-259pp.
- Soltani. B., Rashtchian, D., Tohidi, B. & Jamialahmadi, M. (2010). **A Novel Method for Mitigation of Asphaltene Deposition in the Wellstring**. Iranian Journal Chemistry and Chemical Engineering, Vol. 29(2). 131-141pp.
- Speight, J. (1992). **Molecular Models for Asphaltenes and Implications for Processing**. Kentuchy University & US DOE EAST oil shale. Samposium Proceedings. 20-28pp.
- Tavakoldavani, M. & Ashoori, S. (2017). **Determination of Asphaltene Deposition Profile in a Wellbores' Column of One Iranian Oil Reservoir**. Journal of Applied Environmental and Biological Sciences. Vol. 7(4). 156-164pp.
- Ting, D. (2003). **Thermodynamic Stability and Phase Behavior of Asphaltenes in Oil and Other Highly Asymmetric Mixtures**. Rice University. Houston, Texas.
- Wang, J., Buckley, J. and PRRC, N.M.T., (2002). **Standard Procedure for Separating Asphaltenes from Crude Oils.** Petroleum Recovery Research Center. New Mexico Tech.1-3pp.
- Wang, M. (2016). **Aggregation Thermodynamics for Asphaltene Precipitation**. American Institute of Chemical Engineers Journal. Vol. 52(4). 1254-1256pp.
- Zhang, D., Kharrat, A., Hammami, A., Akbarzadeh, K., Allenson, S., Creek, J., Kabir, S., Marshal, A., Rodgers, R., Mullins, O. & Solbakken, T. (2007). **Asphaltenes- Problematic but Rich in Potential**. Oil Field Review. 22-26pp

- Zhang, X., Pedrosa, N. & Moorwood, T. (2012). **Modeling Asphaltene Phase Behavior: Comparison of Methods for Flow Assurance Studies**. Energy & Fuels Article. Vol. 26. 2611-2620pp. dx.doi.org/10.1021/ef201383r.
- Zubair, C., Ramasamy, M. & Mukhtar, H. (2015). **Temperature Effects on Solubility of Asphaltene in Crude Oils**. Chemical Engineering Research and Design. Vol. 94. 573-583pp.

APPENDICES

Appendix A: IP 143/01 standard procedure



**Mixture* = oil + n-heptane

***Precipitated* = asphaltene + inorganic material + wax

Figure 32: IP 143 Standard procedure for determination of asphaltene content.

Appendix B: ASTM D2007-11 procedure method for SARA determination (modified method).

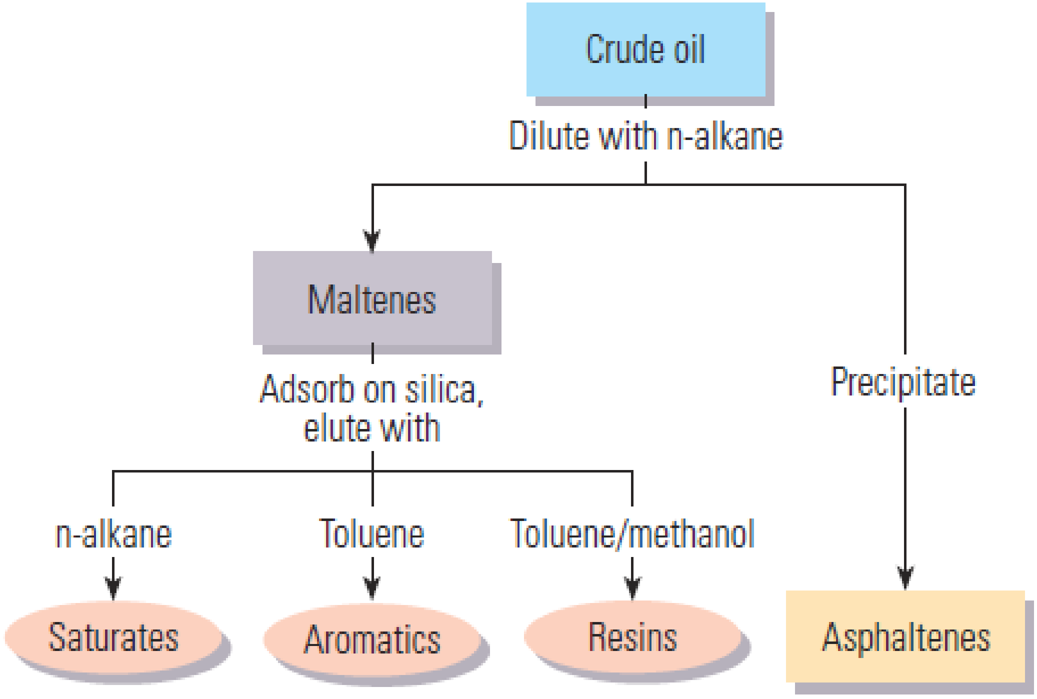


Figure 33: Crude oil separation. (Zhang, D. *et al.*, 2007; ASTM D2007-11 standard method).